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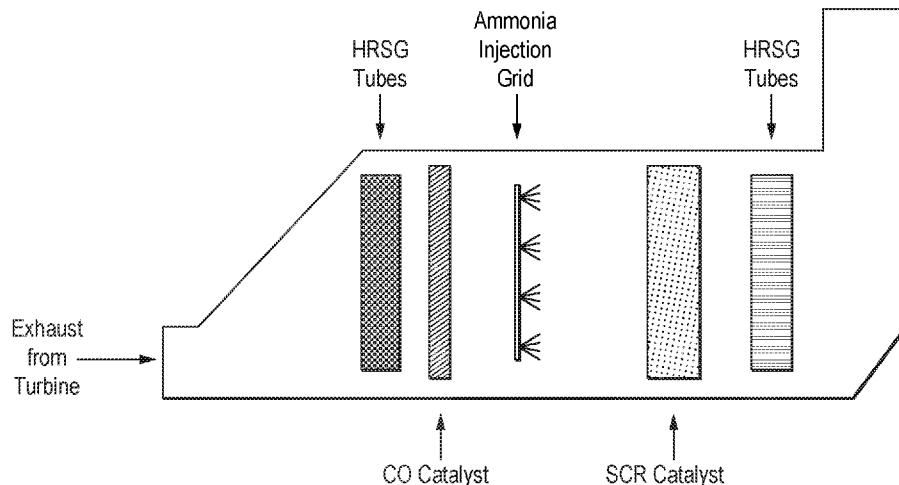


FIG. 1

(57) Abstract: A method of extending the useful life of an aged selective catalytic reduction (SCR) catalyst bed, which catalyses the conversion of oxides of nitrogen (NO_x) to dinitrogen (N₂) in the presence of a nitrogenous reductant, in the exhaust gas after treatment system of a stationary source of NO_x so that the exhaust gas emitted to atmosphere from the system continues to meet proscribed limits for both NO_x and ammonia emissions, which method comprising the step of retrofitting an additional honeycomb substrate monolith or a plate-type substrate comprising a catalyst (ASC) for converting ammonia in exhaust gas also containing oxygen to nitrogen and water downstream of the aged SCR catalyst bed, wherein the kNO_x of the honeycomb substrate monolith comprising the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water is greater than or equal to 80 m/hr between 300 and 400°C inclusive, wherein kNO_x of a sample of the catalyst, which has been aged at

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**METHOD OF EXTENDING THE USEFUL LIFE OF AN AGED SCR CATALYST
BED IN AN EXHAUST SYSTEM OF A STATIONARY SOURCE OF NO_x**

5 The present invention relates to a method of extending the useful life of an aged selective catalyst reduction catalyst bed in an exhaust system of a stationary source of NO_x.

Modern electric power generators fuelled by natural gas, light distillates or syngases (derived e.g. from coal) operate combined cycle gas turbines, in which the gas is combusted in a gas turbine to generate electricity in a first cycle and heat generated from combustion of the 10 gas is recovered in a steam-operated heat engine in a second cycle. The combination of these two cycles increases the net overall efficiency of the system. The second cycle is typically conducted in what is known as a Heat Recovery Steam Generator (HRSG) system, which typically also includes catalytic components for treating components including oxides of nitrogen (NO_x), carbon monoxide (CO) and unburned hydrocarbons (HC) in the exhaust gas 15 resulting from the combustion of the gas in the first cycle. Catalytic activity of these catalytic components is promoted by transfer of the heat of the exhaust gas being treated to the catalytic components themselves. Location of the catalytic components within the HRSG system can be selected for temperature-optimised catalytic activity.

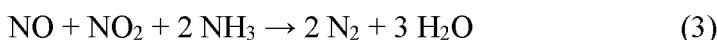
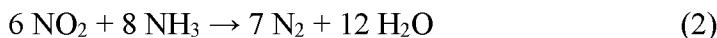
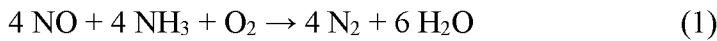
20 Emission of NO_x from stationary sources, primarily from power stations, industrial heaters, cogeneration plants including wood-fired boilers, stationary diesel and gas engines, marine propulsion engines, diesel locomotive engines, industrial and municipal waste incinerators, chemical plants and glass, steel and cement manufacturing plants represents a major environmental problem. NO_x leads to the formation of ozone in the troposphere, the 25 production of acid rain and respiratory problems in humans. NO_x is formed thermally in the combustion process by combination of the N₂ and O₂ present in the air. At temperatures greater than about 1,500 °C, this reaction proceeds at appreciable rates through a well-characterised mechanism called the Zeldovich mechanism.

30 In order to meet NO_x emissions standards specified by various regulatory agencies, methods of after-treatment of exhaust (flue) gases are required. Among such after-treatment methods, the selective catalytic reduction (SCR) method is the best developed and most used world-wide for the control of NO_x emissions from stationary sources due to its efficiency,

selectivity (to N₂ product) and economics. The SCR reaction generally consists of the reduction of NO_x by ammonia (NH₃) to form water and nitrogen.

The major reactions involved in SCR NO_x reduction are shown in reactions (1), (2) and

5 (3):



10

Three types of catalysts that promote reactions (1)-(3) inclusive have been developed: noble metals, metal oxides and metal promoted zeolites. Noble metal SCR catalysts are primarily considered for low temperature and natural gas applications, because they can undesirably promote SO₂ oxidation at above about 200°C.

15

Among the various metal oxide SCR catalysts developed for 300-400°C applications, vanadia supported on titania in the anatase form and promoted with tungsta or molybdena was found to resist sulfation and to have low activity for the SO₂ oxidation reaction.

20

Commercial zeolite SCR catalysts for the treatment of stationary source NO_x emissions include mordenite (see R.H. Heck et al, "Catalytic Air Pollution Control – Commercial Technology", 3rd Edition (2009) John Wiley & Sons, Inc. Hoboken, New Jersey). See in particular Chapter 12.

25

Fe-promoted zeolite catalysts have been proposed for SCR primarily for use in gas-fired cogeneration plants at high temperatures, i.e. up to 600°C, where metal oxide catalysts can be thermally unstable.

30

The commercial SCR catalysts are deployed in the form of extruded honeycomb

monoliths, plates or as coatings on inert honeycomb monoliths.

For a more complete description of the background to the application of the SCR method to stationary sources of NO_x emission, please see P. Forzatti, App. Cat A: General 222 (2001) 221-236.

Reaction (3) is known to be a relatively fast reaction compared to either reaction (1) or in particular reaction (2), and so is preferred. A suitable oxidation catalyst disposed upstream of the SCR catalyst for this purpose is also relevant for treating CO and HC components in the 5 exhaust gas. Reductant injection upstream of the SCR catalyst is generally done downstream of the oxidation catalyst to avoid inefficient consumption of ammonia (by oxidation to NO_x), with consequent reduction of overall system conversion performance. Ammonia injection can be done via a suitable apparatus, such as an ammonia injection grid (AIG).

10 Although any of the above SCR catalysts can be used to treat NO_x in a HRSG system, gas combustion exhaust gas temperatures generally require that the above-mentioned metal oxide or metal promoted zeolites are appropriate.

15 Gas turbine emission control systems generally include a CO oxidation catalyst (CO-Ox) followed by an ammonia injection grid (AIG) and finally an SCR catalyst bed (SCR). As the catalyst system ages, CO conversions drop and SCR performance deteriorates. To maintain system overall NO_x emissions to at or below a pre-defined minimum, the plant operator increases the ammonia:NO_x ratio to continue to drive reactions (1), (2) and (3). However, this increases ammonia emissions (“slip”) and increases the cost of operation through consumption 20 of reductant. Ammonia slip refers to emissions of unreacted ammonia that result from incomplete reaction of the NO_x and the reductant. Ammonia slip may cause formation of ammonium sulfates, which can plug or corrode downstream components and contribute undesirably to particulate matter (PM2.5) emissions to atmosphere. In the U.S., permitted ammonia slip levels are typically 2 to 10 ppm.

25

Eventually, the SCR catalyst activity deteriorates to the point where the ammonia:NO_x ratio can no longer be increased without exceeding the pre-defined maximum. At this point, typical practice is to remove and dispose of the spent catalysts and replace with new catalyst so that the system is able to remain compliant with emission standards.

30

The inventors have now discovered, very surprisingly, that the ability of an end-of-life SCR catalyst bed in an exhaust system of a gas turbine to treat NO_x to within proscribed limits can be extended by up 50% without exceeding proscribed NH₃ slip limits by retrofitting a catalyst for treating ammonia slip (referred to as an ammonia slip catalyst or “ASC” herein)

downstream of the end-of-life SCR catalyst bed more economically than by replacing the end-of-life SCR catalyst itself. This discovery has the considerable advantage that the benefit can be obtained using a relatively small catalyst volume compared with the SCR catalyst bed volume and consequently additional backpressure added to the system is negligible and does

5 not significantly affect overall power generation efficiency.

According to one aspect, the invention provides a method of extending the useful life of an aged selective catalytic reduction (SCR) catalyst bed, which catalyses the conversion of oxides of nitrogen (NO_x) to dinitrogen (N_2) in the presence of a nitrogenous reductant, in the

10 exhaust gas after treatment system of a stationary source of NO_x so that the exhaust gas emitted to atmosphere from the system continues to meet proscribed limits for both NO_x and ammonia emissions, which method comprising the step of retrofitting a honeycomb substrate monolith or a plate-type substrate comprising a catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water downstream of the aged SCR catalyst bed, wherein the

15 $k\text{NO}_x$ of the honeycomb substrate monolith comprising the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water is greater than or equal to about 80 m/hr between about 250 and about 400°C inclusive, wherein $k\text{NO}_x$ of a sample of the catalyst, which has been aged at 450°C in 10% H_2O (as steam) in air for 48 hours, is determined by a SCR activity test in a laboratory scale reactor using a gas composition of 50 ppm CO , 30 ppm

20 NO , 36 ppm NH_3 , 15% O_2 , 8% water, 3% CO_2 , balance N_2 .

The invention provides a number of significant advantages. The useable life of the SCR catalyst can be extended by up to two times. This promotes sustainable use of resources in that the relatively large SCR catalyst volume does not have to be recycled or sent to landfill

25 for a significant period of time.

In practice, the relatively small volume of the retrofitted honeycomb substrate monolith or plate-type substrate comprising the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water is just one of the factors enabling the retrofitted

30 catalyst to be manufactured at a lower cost than the replacement cost of the SCR catalyst. The cost of the retrofitted catalyst can be more than 20% cheaper than the SCR catalyst replacement cost.

An ammonia slip catalyst is designed selectively to promote the following overall reaction:



5

As described in greater detail hereinbelow, US patent application publication nos. 2007/0110643 A1, 2016/0245139 A1 and 2016/0256823 A1 propose the use of an ammonia slip catalyst (also known as an ammonia oxidation (“AMOX”) catalyst) downstream from or in combination with a SCR catalyst in an exhaust system of a gas turbine engine.

10

However, electric power generation plant operators generally do not include ammonia slip catalysts downstream from newly installed SCR catalyst beds because the SCR catalyst bed is able to convert NOx at negligible ammonia slip and in any event it is permitted to emit relatively low levels of ammonia to atmosphere, as described hereinabove. Therefore, the 15 addition of an ammonia slip catalyst in the systems proposed by these publications is unnecessary and undesirably increases the economic cost and burden to the plant operator of installing the system.

US patent application publication no. 2007/0110643 A1 discloses an exhaust gas 20 treatment apparatus for reducing the concentration of NOx, HC and CO in an exhaust gas stream such as produced by a gas turbine engine of a power generating station. The treatment apparatus includes a multifunction catalytic element having an upstream reducing-only portion and a downstream reducing-plus-oxidizing portion that is located downstream of an ammonia injection apparatus. The selective catalytic reduction (SCR) of NOx is promoted in 25 the upstream portion of the catalytic element by the injection of ammonia in excess of the stoichiometric concentration, with the resulting ammonia slip being oxidized in the downstream portion of the catalytic element. Any additional NOx generated by the oxidation of the ammonia is further reduced in the downstream portion before being passed to the atmosphere.

30

US patent application publication no. 2016/0245139 A1 discloses an exhaust system for a power generating apparatus comprising a heat source for combusting a fuel in air to produce power, which exhaust system being adapted to receive a flowing exhaust gas and comprising a catalyst system for treating the exhaust gas, which catalyst system comprising a

first oxidation catalyst and a second catalyst, wherein the first oxidation catalyst is positioned downstream from the heat source so that the flowing exhaust gas contacts the first oxidation catalyst before the second catalyst.

5 US patent application publication no. 2016/0256823 A1 discloses a system including a nitrogen oxide reduction catalyst fluidly coupled to an exhaust conduit of an engine system. The nitrogen oxide reduction catalyst is configured to reduce nitrogen oxides in an engine exhaust. The system also includes an ammonia oxidation catalyst fluidly coupled to the exhaust conduit downstream of the nitrogen oxide reduction catalyst and configured to reduce 10 ammonia in the engine exhaust. Further, the system includes a reductant injection control system configured to control an injection of reductant into the exhaust conduit, determine a first nitrogen oxide conversion rate of the nitrogen oxide reduction catalyst, determine an ammonia storage value of the nitrogen oxide reduction catalyst, and determine a first temperature of the engine exhaust upstream of the ammonia oxidation catalyst. The reductant 15 injection control system is also configured to increase or decrease the injection of reductant based on the first nitrogen oxide conversion, the ammonia storage value, and the first temperature.

US patent publication no. 7727499 discloses a method for removal by oxidation of the 20 excess ammonia (NH_3) gas (“ammonia slip”) resulting from flue and exhaust gases that have been subjected to selective catalytic reduction (SCR) for reduction of nitrogen oxides (NO_x) with ammonia. More specifically, the method uses an ammonia oxidation catalyst consisting of a zeolite, one or more precious metals, and a base metal compound, to catalyze the 25 oxidation of both ammonia and carbon monoxide (CO), while minimizing the formation of nitrogen oxides (NO_x).

The rate constant $k\text{NO}_x$ is defined as follows:

Rate constant ($k\text{NO}_x$ (m/hr)) = -area velocity (A_v (m/hr)) * $\ln(1-\text{NO}_x \text{ conversion}/100)$,
30 where the area velocity A_v (m/hr) = Q (volumetric flow rate (m³/hr)) / A_{cat} (catalyst surface area (m²)).

It can be seen from these equations that the $k\text{NO}_x$ constant for a catalyst is independent of the pitch (or cells per square inch) of the honeycomb substrate monolith or a

plate-type substrate and therefore also the volume of the honeycomb substrate monolith or a plate-type substrate.

In practice, it is desirable that the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water, i.e. the ammonia slip catalyst (ASC), has as low a pressure drop as economically possible. This is because the addition of the ASC in the system creates additional pressure drop that requires additional energy input to accommodate, compared with the system including the SCR catalyst alone. This additional energy input can be important for gas turbine power generation as any additional energy demands in the system can reduce the efficiency of the power generation cycle as a whole.

An important component of pressure drop is the depth of the ASC bed. The depth of the ASC bed can be influenced, for example, by the temperature of operation, the kNO_x and the pitch (or honeycomb cell density) of the substrate monolith comprising the ASC. So, for example, for a fixed ASC pitch, by lowering the kNO_x, the more geometric ASC surface area – and therefore substrate monolith volume and resulting increased backpressure – is required to compensate.

Similarly, by lowering the pitch of the ASC substrate monolith, an increased catalyst volume would be required to compensate and maintain a fixed kNO_x.

Therefore, depending on the location of the ASC in the system and the temperature of the catalyst in use, there is a balance to be struck between at least the pitch of the substrate monolith, the volume of the substrate monolith, the geometric surface area of the substrate monolith and the composition of the ASC, the selection of which parameters can be determined based on cost and operational considerations and are embraced generically by the kNO_x.

The kNO_x of the honeycomb substrate monolith or the plate-type substrate comprising the catalyst can be less than or equal to about 300 m/hr.

30

Preferably, the kNO_x of the honeycomb substrate monolith or the plate-type substrate comprising the catalyst is about $90 < \text{kNO}_x < \text{about } 300 \text{ m/h}$ between about 300 and about 400°C.

The catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water preferably converts about 70% NH₃ at above 250°C, more preferably > about 80% NH₃ at above about 300°C.

5 The catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water preferably has an sNO_x = NO_x out divided by (NH₃ in minus NH₃ out) < about 20% below about 400°C, more preferably an sNO_x < about 10% below about 350°C, wherein the sNO_x is determined using the same conditions defined for determining kNO_x hereinabove.

10

The space velocity at which the exhaust gas contacts the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water can be from 50,000 to 500,000 h⁻¹, such as 100,000 to 400,000 h⁻¹ or 150,000 h⁻¹ to 350,000 h⁻¹.

15

The retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water preferably comprises a platinum group metal supported on a refractory oxide support and a selective catalytic reduction catalyst.

20

The platinum group metal in the platinum group metal supported on a refractory oxide support is loaded to about 1 to about 40 g/ft³, preferably about 1 to about 25 g/ft³ or about 1 to about 10 g/ft³. Lower platinum group metal loadings are preferred because such loadings promote selectivity for reaction (4).

25

The SCR catalyst in the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water can comprise (i) vanadia supported on titania in the anatase form and promoted with tungsta or molybdena; (ii) a metal promoted molecular sieve; or (iii) a mixture of vanadia supported on titania in the anatase form and promoted with tungsta or molybdena and a metal promoted molecular sieve.

30

Where the SCR catalyst in the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water comprises a metal promoted molecular sieve, preferably the molecular sieve is an aluminosilicate zeolite.

Preferably, where the SCR catalyst in the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water comprises a metal promoted molecular sieve, the molecular sieve has a maximum ring size of eight tetrahedral atoms and is

5 further preferably selected from the group consisting of the Framework Type Codes CHA, AEI and AFX. Aluminosilicate zeolites that are particularly durable to hydrothermal ageing and hydrocarbon “coking” have a maximum ring size of eight tetrahedral atoms and are referred to in the art as “small pore” zeolites. Zeolites are categorised by the International Zeolite Association by their Framework Types. However, in certain applications where durability over

10 an extended period is not a primary requirement, e.g. in relatively low temperature applications, “medium pore” zeolites, such as those having the Framework Type Codes MFI or FER or “large pore” zeolites, e.g. BEA or MOR, may be equally applicable.

A silica-to-alumina ratio (SAR) of the zeolite can be any appropriate SAR for

15 promoting the reactions (1), (2) and (3). Generally, this is a balance between thermal stability on the one hand, wherein a relatively high silica content is preferred, and the promoting effect of an ion-exchanged transition metal, wherein a relatively high alumina content is preferred. In practice, the SAR selected may be dependent on the framework type code of the zeolite, but is typically within the range of about 10 to about 256, with SAR of about 15 to about 40 preferred

20 for small pore zeolites such as CHA, AEI and AFX.

Preferably, the metal in the metal promoted molecular sieve is copper and/or iron.

The refractory oxide support for the platinum group metal in the SCR catalyst in the

25 retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water can be silica-doped alumina, titania or optionally doped zirconia.

The honeycomb substrate monolith or the plate-type substrate in the SCR catalyst in the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen

30 and water has an axial length and can be coated with a first washcoat layer comprising the platinum group metal supported on a refractory oxide support and a second washcoat layer comprising the SCR catalyst.

The first washcoat layer can be disposed in a first zone coated from a first end of the honeycomb substrate monolith and the second washcoat layer can be disposed in a second zone coated from a second end of the honeycomb substrate monolith or the plate-type substrate, wherein the second layer is disposed upstream from the first layer.

5

Alternatively, the first zone is less than the axial length of the honeycomb substrate monolith or the plate-type substrate and the second layer of the second zone at least partially overlies the first layer. In this case, preferably the second layer can extend to the entire axial length of the honeycomb substrate monolith or the plate-type substrate.

10

Alternatively, the first layer can extend to the entire axial length of the honeycomb substrate monolith or the plate-type substrate and the second layer can overlie the first layer and can extend to the entire axial length of the honeycomb substrate monolith or the plate-type substrate.

15

Preferably, the proscribed limit for NOx emissions in the method according to the invention is less than or equal to 2 ppm and/or the proscribed limit for ammonia emissions is less than or equal to 10 ppm, such as less than 5 ppm or less than 2 ppm.

20

The temperature at which the exhaust gas contacts the SCR catalyst bed can be about 200°C to about 450°C.

25

The nitrogenous reductant is ammonia (NH₃) *per se*, hydrazine or any suitable ammonia precursor, such as urea ((NH₂)₂CO), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate or ammonium formate. It is important that the mixing of ammonia and the exhaust gas is done as completely as possible before the exhaust gas/ammonia enters the SCR catalyst. This can be done using various baffles and static mixers having e.g. herringbone and skew channel shapes, as necessary provided that they do not significantly contribute to an increase in backpressure. Good mixing of ammonia and exhaust gas can be promoted by a thorough two dimensional coverage of reducing agent injection across a duct carrying the exhaust gas. Such arrangements are known in the art as ammonia injection grids (AIG).

30

In order to promote reaction (3) (and reactions (1) and (2) in addition), the alpha ratio of ammonia molecules to NO_x molecules used in the reaction is preferably about 0.90 to about 2.00, preferably < about 1.8, such as about 0.95 to about 1.5 or 1.00 to about 1.20.

5 The SCR catalyst can be in the form of a washcoat that is coated onto a substrate, such as an inert ceramic honeycomb monolith, e.g. made from cordierite, or a metal monolith or it can be prepared as an extruded honeycomb body, wherein the catalyst is mixed with a paste of binder (or matrix) components and then extruded into the desired shape having flow channels extending therethrough. Washcoat compositions containing the zeolites for use in the present 10 invention for coating onto the monolith substrate or manufacturing extruded type substrate monoliths can comprise a binder selected from the group consisting of alumina, silica, (non-zeolite) silica-alumina, naturally occurring clays, TiO₂, ZrO₂, and SnO₂.

15 In particular, the SCR catalyst can be any of those described for use in the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water described hereinabove, i.e. one of:

- (i) vanadia supported on titania in the anatase form and promoted with tungsta or molybdena;
- (ii) a metal promoted molecular sieve; or
- 20 (iii) a mixture of vanadia supported on titania in the anatase form and promoted with tungsta or molybdena and a metal promoted molecular sieve.

25 The method according to the invention can be used to treat exhaust gas from any stationary source of NO_x emission. In particular, the exhaust gas can be a product of a power station, an industrial heater, a cogeneration power plant, a combined cycle power generation plant, a wood-fired boiler, a stationary diesel engine, a stationary natural gas-fired engine, a marine propulsion engine, a diesel locomotive engine, an industrial waste incinerator, a municipal waste incinerator, a chemical plant, a glass manufacturing plant, a steel manufacturing plant or a cement manufacturing plant.

30

In a preferred application, the exhaust gas is a product of a cogeneration plant, preferably a stationary natural gas-fired engine.

Preferably, the exhaust gas aftertreatment system comprises a heat recovery steam generator (HRSG).

The term “comprising” as used herein can be exchanged for the definitions “consisting essentially of” or “consisting of”. The term “comprising” is intended to mean that the named elements are essential, but other elements may be added and still form a construct within the scope of the claim. The term “consisting essentially of” limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. The term “consisting of” closes the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith.

For the avoidance of doubt, the entire contents of all documents cited herein are incorporated herein by reference.

15

A prior art HRSG exhaust system for a gas turbine including a SCR catalyst is illustrated in the Figure 1, which in Figure 2 has been adapted to the method according to the present invention by insertion of an ammonia slip catalyst downstream of the SCR catalyst in the location illustrated. Figures 1 and 2 are self-explanatory.

20

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only.

EXAMPLES

25

Example 1

A dual layered Ammonia Slip Catalyst (ASC) was prepared on a ceramic 230 cells per square inch (cpsi) honeycomb substrate monolith having 7 mil (thousandths of an inch) cell wall thickness. A first (lower) layer was coated directly onto the substrate having a 30 continuous alumina washcoated layer along the entire axial length of the substrate. The resulting coated part was dried and calcined. Next Pt was impregnated into the washcoated alumina layer from a platinum nitrate solution to a loading of 5g/ft³ Pt. The resulting part was then dried and calcined. Finally, a second washcoat layer comprising Cu impregnated CHA zeolite mixed with binders was applied in a continuous layer covering 100% of Pt

alumina layer along the entire axial length of the substrate and the resulting part was then dried and calcined. A cylindrical core of 2 inches in diameter and 3.3 inches in length was cut from the finished honeycomb substrate monolith coated with the dual layered ASC.

5

Example 2 (SCR Test)

The cylindrical ASC core of Example 1 was degreened at 450°C in 10% H₂O (as steam) in air for 48 hours then activity tested in a laboratory scale reactor for SCR activity. The gas composition fed to the catalyst for the activity test was 50 ppm CO, 30 ppm NO, 36 ppm NH₃, 15% O₂, 8% water, 3% CO₂, and balanced by N₂. CO, NOx, and NH₃ conversions were measured with the reactor held at steady state temperature points ranging from 200 to 450°C. The Gas Hourly Space Velocity (GHSV) over the ASC volume was 180,000 hr⁻¹.

The CO conversion, NOx conversion, and NH₃ conversion are each shown in Table 1 for the various temperatures. The kNOx, defined as $kNOx = - (Area\ Velocity) * \ln(1-NOx\ Conversion/100)$, are also shown.

TABLE 1

Temp °C	NO Conv (%)	CO Conv (%)	NH ₃ Conv (%)	kNOx
200	40	41	35	46
252	64	56	73	94
305	73	64	84	120
352	75	67	87	125
402	71	70	87	113
452	59	73	86	80

Example 3 (NH₃ Oxidation Test)

The cylindrical ASC core of Example 1 was degreened at 450°C in 10% H₂O in air for 48 hours then activity tested in a laboratory scale reactor for NH₃ oxidation activity. The gas composition fed to the catalyst was 50 ppm CO, 30 ppm NH₃, 10% O₂, 4% water, 3% CO₂, and balanced by N₂. CO, NOx, and NH₃ conversions were measured with the reactor held at steady state temperature points ranging from 200 to 450°C. The Gas Hourly Space Velocity (GHSV) over the ASC volume was 120,000 hr⁻¹.

The results show CO conversion and NH₃ conversion in Table 2. The sNOx, defined as (NOx out divided by (NH₃ in minus NH₃ out)), is also shown.

TABLE 2

Temp °C	NH ₃ Conv. (%)	CO Conv. (%)	sNOx (%)
200	44	46	2
250	78	72	3
298	88	80	4
345	91	83	6
401	92	86	8
451	92	88	18

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Example 4 (SCR Test w/high ammonia to NOx ratio (ANR))

The cylindrical ASC core of Example 1 was degreened at 450°C with 10% H₂O in air for 48 hours then activity tested in a laboratory scale reactor for SCR activity. The gas composition fed to the catalyst for the activity test was 50 ppm CO, 30 ppm NO, 54 ppm NH₃, 15% O₂, 8% water, 3% CO₂, and balanced by N₂. CO, NOx, and NH₃ conversions were measured with the reactor held at steady state temperature points ranging from 200 to 450°C. The Gas Hourly Space Velocity (GHSV) over the ASC volume was 180,000 hr⁻¹.

The CO conversion, NOx conversion, and NH₃ conversion are shown in Table 1 for the various temperatures. The kNOx, defined as kNOx = - (Area Velocity) * ln (1-NOx Conversion/100), are also shown.

TABLE 3

Temp °C	NO Conv	CO Conv	NH ₃ Conv	kNOx
200	46	46	30	56
253	67	59	70	101
305	73	66	81	120
353	76	69	86	128
402	73	71	87	118
452	63	74	88	90

CLAIMS:

1. A method of extending the useful life of an aged selective catalytic reduction (SCR) catalyst bed, which catalyses the conversion of oxides of nitrogen (NO_x) to dinitrogen (N₂) in the presence of a nitrogenous reductant, in the exhaust gas after treatment system of a stationary source of NO_x so that the exhaust gas emitted to atmosphere from the system continues to meet proscribed limits for both NO_x and ammonia emissions, which method comprising the step of retrofitting a honeycomb substrate monolith or a plate-type substrate comprising a catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water downstream of the aged SCR catalyst bed, wherein the kNO_x of the honeycomb substrate monolith comprising the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water is greater than or equal to about 80 m/hr between about 250 and about 400°C inclusive, wherein kNO_x of a sample of the catalyst, which has been aged at 450°C in 10% H₂O (as steam) in air for 48 hours, is determined by a SCR activity test in a laboratory scale reactor using a gas composition of 50 ppm CO, 30 ppm NO, 36 ppm NH₃, 15% O₂, 8% water, 3% CO₂, balance N₂.
2. A method according to claim 1, wherein the kNO_x of the honeycomb substrate monolith or the plate-type substrate comprising the catalyst is less than or equal to about 300 m hr.
3. A method according to claim 1 or 2, wherein the kNO_x of the honeycomb substrate monolith or the plate-type substrate comprising the catalyst is about 90 < kNO_x < about 300 m/h between about 300 and about 400°C
4. A method according to claim 1, 2 or 3, wherein the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water converts > about 70% NH₃ at above about 250°C.
5. A method according to claim 4, wherein the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water converts > about 80% NH₃ at above about 300°C.

6. A method according to any preceding claim, wherein the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water has an sNO_x = NO_x out divided by (NH₃ in minus NH₃ out) < about 20% below about 400°C, wherein the sNO_x is determined using the same conditions defined in claim 1 for determining kNO_x.

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7. A method according to claim 6, wherein the catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water has an sNO_x < about 10% below about 350°C.

10 9. A method according to any preceding claim, wherein the space velocity at which the exhaust gas contacts the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water is from 50,000 to 500,000 h⁻¹.

15 10. A method according to any preceding claim, wherein the retrofitted catalyst for converting ammonia in exhaust gas also containing oxygen to nitrogen and water comprises a platinum group metal supported on a refractory oxide support and a selective catalytic reduction catalyst.

20 11. A method according to claim 10, wherein the platinum group metal in the platinum group metal supported on a refractory oxide support is loaded to about 1 to about 40 g/ft³.

12. A method according to claim 10 or 11, wherein the SCR catalyst is vanadia supported on titania in the anatase form and promoted with tungsta or molybdena.

25 13. A method according to claim 10 or 11, wherein the SCR catalyst is a metal promoted molecular sieve.

30 14. A method according to claim 10 or 11, wherein the SCR catalyst comprises a mixture of vanadia supported on titania in the anatase form and promoted with tungsta or molybdena and a metal promoted molecular sieve.

15. A method according to claim 13 or 14, wherein the molecular sieve is an aluminosilicate zeolite.

16. A method according to claim 13, 14 or 15, wherein the molecular sieve has a maximum ring size of eight tetrahedral atoms.

17. A method according to claim 13, 14, 15 or 16, wherein the molecular sieve has a
5 Framework Type Code that is CHA, AEI or AFX.

18. A method according to claim 13, 14 or 15, wherein the molecular sieve has a
Framework Type Code BEA, MOR, MFI or FER.

10 19. A method according to any of claims 13 to 18, wherein the metal in the metal promoted molecular sieve is copper and/or iron.

20. A method according to any of claims 10 to 19, wherein the refractory oxide support for the platinum group metal is silica-doped alumina, titania or optionally doped zirconia.

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21. A method according to any of claims 10 to 20, wherein the honeycomb substrate monolith or the plate-type substrate has an axial length and is coated with a first washcoat layer comprising the platinum group metal supported on a refractory oxide support and a second washcoat layer comprising the SCR catalyst.

20

22. A method according to claim 21, wherein the first layer is disposed in a first zone coated from a first end of the honeycomb substrate monolith and the second layer is disposed in a second zone coated from a second end of the honeycomb substrate monolith or the plate-type substrate, wherein the second layer is disposed upstream from the first layer.

25

23. A method according to claim 22, wherein the first zone is less than the axial length of the honeycomb substrate monolith or the plate-type substrate and the second layer of the second zone at least partially overlies the first layer.

30 24. A method according to claim 22, wherein the second layer extends to the entire axial length of the honeycomb substrate monolith or the plate-type substrate.

25. A method according to claim 21, wherein the first layer extends to the entire axial length of the honeycomb substrate monolith and the second layer overlies the first layer and

extends to the entire axial length of the honeycomb substrate monolith or the plate-type substrate.

26. A method according to any preceding claim, wherein the proscribed limit for NO_x 5 emissions is less than or equal to 2 ppm.

27. A method according to any preceding claim, wherein the proscribed limit for ammonia emissions is less than or equal to 10 ppm.

10 28. A method according to any preceding claim, wherein the temperature at which the exhaust gas contacts the SCR catalyst bed is about 200°C to about 450°C.

29. A method according to any preceding claim, wherein the nitrogenous reductant is ammonia (NH₃).

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30. A method according to any preceding claim, wherein an alpha ratio of ammonia molecules to NO_x molecules contacting the aged SCR catalyst bed is about 0.90 to about 2.00.

20 31. A method according to any preceding claim, wherein the stationary source of NO_x is a power station, an industrial heater, a cogeneration power plant, a combined cycle power generation plant, a wood-fired boiler, a stationary diesel engine, a stationary natural gas-fired engine, a marine propulsion engine, a diesel locomotive engine, an industrial waste incinerator, a municipal waste incinerator, a chemical plant, a glass manufacturing plant, a steel manufacturing plant or a cement manufacturing plant.

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32. A method according to any of claims 1 to 30, wherein the exhaust gas is a product of a cogeneration plant, preferably a stationary natural gas-fired engine.

30 33. A method according to claim 31 or 32, wherein the exhaust gas after treatment system comprises a heat recovery steam generator (HRSG).

34. A method according to any preceding claim, wherein the SCR catalyst is a washcoat coated onto a substrate or is a component of an extruded honeycomb body.

35. A method according to claim 34, wherein the SCR catalyst is one of:

- (i) vanadia supported on titania in the anatase form and promoted with tungsta or molybdena;
- (ii) a metal promoted molecular sieve; or
- (iii) a mixture of vanadia supported on titania in the anatase form and promoted with tungsta or molybdena and a metal promoted molecular sieve.

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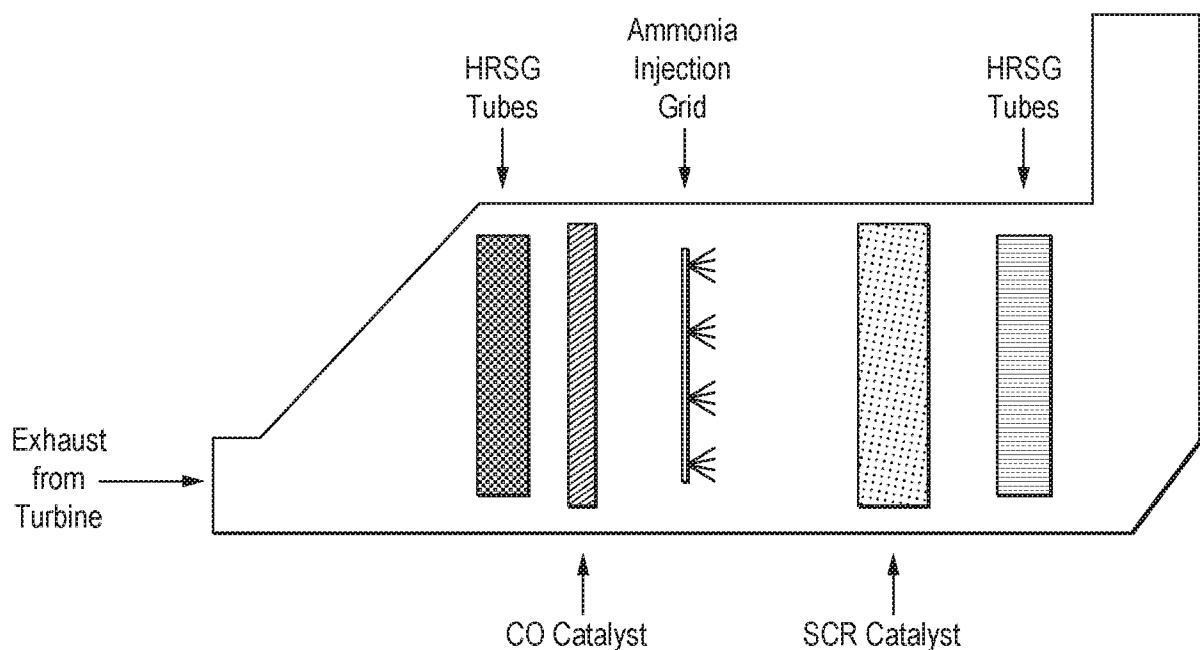


FIG. 1

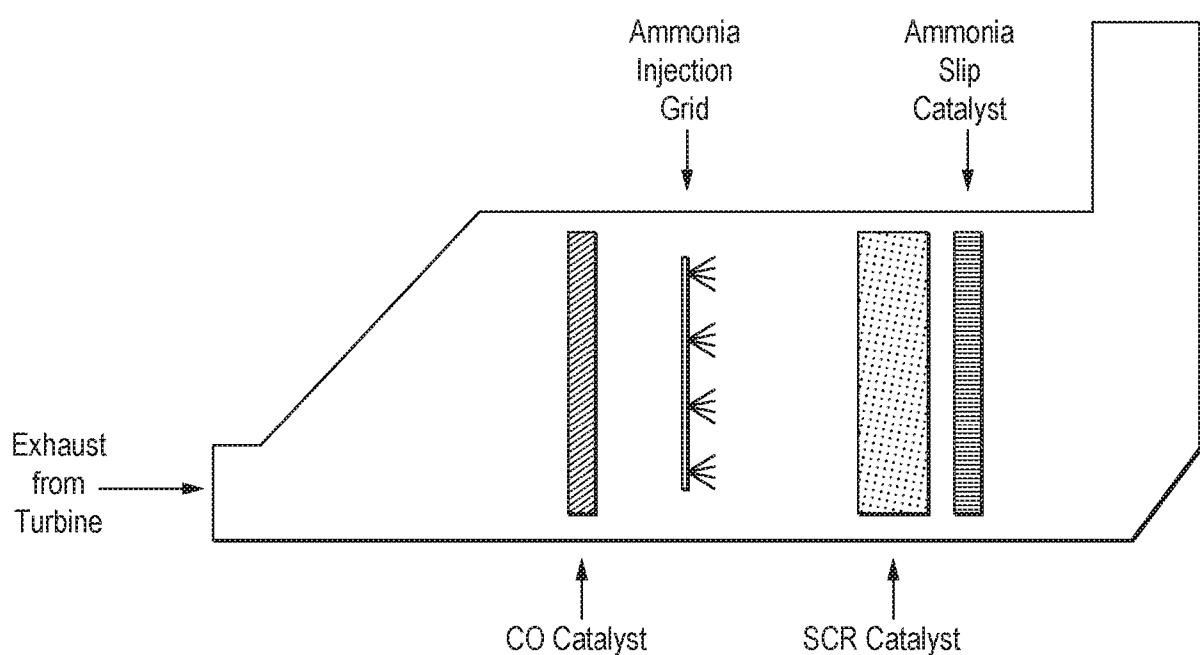


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/053599

A. CLASSIFICATION OF SUBJECT MATTER
INV. F01N3/20 F01N13/00 F01N3/10 F02C3/30
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)
F01N F02C

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014/260199 A1 (GRZESIAK REBECCA [US]; ET AL) 18 September 2014 (2014-09-18) paragraphs [0015], [0016]; figure 2 -----	1-31
A	GB 2 538 132 A (JOHNSON MATTHEY PLC [GB]) 9 November 2016 (2016-11-09) page 10, lines 7-15; figure 3 -----	1-35
A	WO 2014/085354 A1 (CORNING INC [US]; GEORGE SAM [US]; HEIBEL ACHIM KARL-ERICH [US]) 5 June 2014 (2014-06-05) paragraphs [0028], [0029], [0064]; figure 1 -----	1-35
A	WO 2011/045252 A1 (BASF SE [DE]; BASF CATALYSTS LLC [US]; BULL IVOR [DE]; MUELLER ULRICH) 21 April 2011 (2011-04-21) the whole document ----- -/-	2-30,34, 35

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
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"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
7 February 2018	19/02/2018
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 Kolland, Ulrich

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/053599

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/083431 A2 (JOHNSON MATTHEY PLC [GB]) 5 June 2014 (2014-06-05) the whole document -----	2-30,34, 35
A	WO 2015/017516 A2 (JOHNSON MATTHEY PLC [GB]; FEDEYKO JOSEPH MICHAEL [US]) 5 February 2015 (2015-02-05) the whole document -----	2-30,34, 35
A	WO 2008/132452 A2 (JOHNSON MATTHEY PLC [GB]; ANDERSEN PAUL JOSEPH [US]; BAILIE JILLIAN EL) 6 November 2008 (2008-11-06) the whole document -----	2-30,34, 35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2017/053599

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 2014260199	A1	18-09-2014	CN 104047697 A		17-09-2014
			DE 102014003639 A1		18-09-2014
			US 2014260199 A1		18-09-2014
<hr/>					
GB 2538132	A	09-11-2016	CN 107223193 A		29-09-2017
			DE 102016102935 A1		25-08-2016
			EP 3259528 A1		27-12-2017
			GB 2538132 A		09-11-2016
			KR 20170118078 A		24-10-2017
			US 2016245139 A1		25-08-2016
			WO 2016132138 A1		25-08-2016
<hr/>					
WO 2014085354	A1	05-06-2014	CN 105378244 A		02-03-2016
			EP 2925978 A1		07-10-2015
			JP 2016505749 A		25-02-2016
			US 2014150409 A1		05-06-2014
			WO 2014085354 A1		05-06-2014
<hr/>					
WO 2011045252	A1	21-04-2011	AR 081475 A1		19-09-2012
			CA 2777507 A1		21-04-2011
			CN 102574116 A		11-07-2012
			EP 2521615 A1		14-11-2012
			JP 5750701 B2		22-07-2015
			JP 2013507321 A		04-03-2013
			KR 20120086711 A		03-08-2012
			RU 2012119164 A		20-11-2013
			US 2012208691 A1		16-08-2012
			US 2016129431 A1		12-05-2016
			WO 2011045252 A1		21-04-2011
<hr/>					
WO 2014083431	A2	05-06-2014	CN 104812486 A		29-07-2015
			DE 112013005743 T5		10-09-2015
			EP 2925441 A2		07-10-2015
			GB 2528378 A		20-01-2016
			JP 2016504183 A		12-02-2016
			KR 20150091343 A		10-08-2015
			RU 2015125904 A		10-01-2017
			US 2014154163 A1		05-06-2014
			WO 2014083431 A2		05-06-2014
<hr/>					
WO 2015017516	A2	05-02-2015	CN 105555403 A		04-05-2016
			DE 102014110811 A1		05-02-2015
			EP 3027309 A2		08-06-2016
			GB 2519403 A		22-04-2015
			GB 2533468 A		22-06-2016
			JP 2016532548 A		20-10-2016
			KR 20160038025 A		06-04-2016
			RU 2016106291 A		31-08-2017
			US 2015037233 A1		05-02-2015
			US 2017189854 A1		06-07-2017
			WO 2015017516 A2		05-02-2015
<hr/>					
WO 2008132452	A2	06-11-2008	BR PI0810133 A2		29-10-2014
			CA 2685009 A1		06-11-2008
			CA 2939726 A1		06-11-2008
			CN 101730575 A		09-06-2010
			CN 102974390 A		20-03-2013
			CN 102974391 A		20-03-2013

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2017/053599

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
	DK	2150328 T3	08-06-2015
	DK	2517775 T3	03-04-2017
	DK	2517776 T3	22-09-2014
	DK	2517778 T3	19-05-2014
	DK	2786796 T3	18-12-2017
	EP	2150328 A2	10-02-2010
	EP	2517773 A2	31-10-2012
	EP	2517774 A2	31-10-2012
	EP	2517775 A2	31-10-2012
	EP	2517776 A1	31-10-2012
	EP	2517777 A2	31-10-2012
	EP	2517778 A1	31-10-2012
	EP	2786796 A1	08-10-2014
	EP	3278863 A1	07-02-2018
	JP	5777339 B2	09-09-2015
	JP	6053734 B2	27-12-2016
	JP	2010524677 A	22-07-2010
	JP	2015027673 A	12-02-2015
	JP	2016195992 A	24-11-2016
	JP	2017060944 A	30-03-2017
	KR	20100017347 A	16-02-2010
	KR	20160142411 A	12-12-2016
	RU	2009143682 A	10-06-2011
	US	2010290963 A1	18-11-2010
	US	2011250127 A1	13-10-2011
	US	2012301378 A1	29-11-2012
	US	2012301379 A1	29-11-2012
	US	2012301380 A1	29-11-2012
	US	2012301381 A1	29-11-2012
	US	2015078968 A1	19-03-2015
	US	2015110682 A1	23-04-2015
	US	2015118114 A1	30-04-2015
	US	2015118115 A1	30-04-2015
	US	2015118121 A1	30-04-2015
	US	2016367939 A1	22-12-2016
	WO	2008132452 A2	06-11-2008