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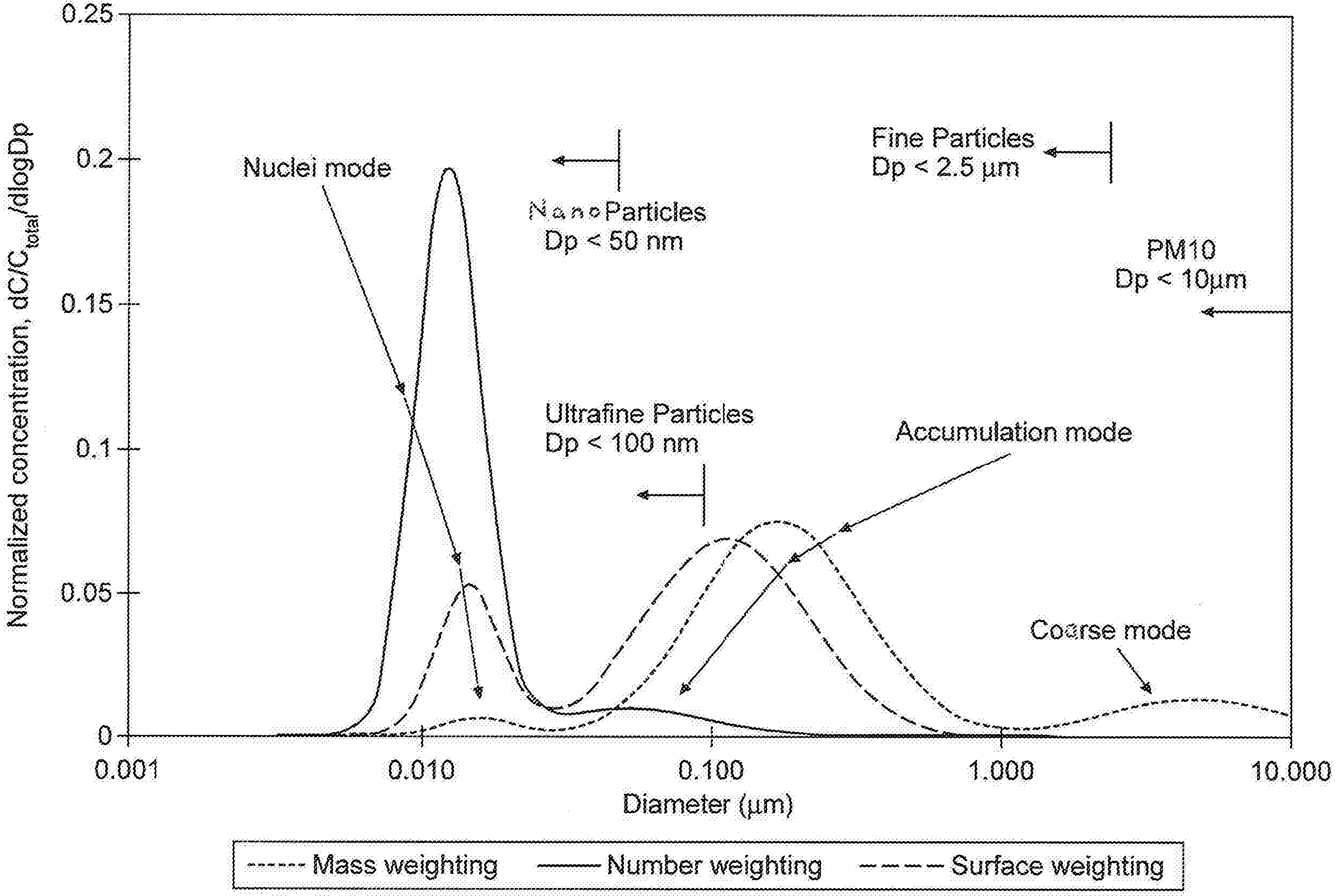
Normalized concentration, $dC/C_{total}/dlogDp$
0.25
0.2
0.15
0.1
0.05
0
0.001
0.010
0.100
1.000
10.000
Diameter (µm)
Nuclei mode
NanoParticles
Dp < 50 nm
Ultrafine Particles
Dp < 100 nm
Fine Particles
Dp < 2.5 µm
PM10
Dp < 10µm
Accumulation mode
Coarse mode
Mass weighting
Number weighting
Surface weighting

FIG. 1

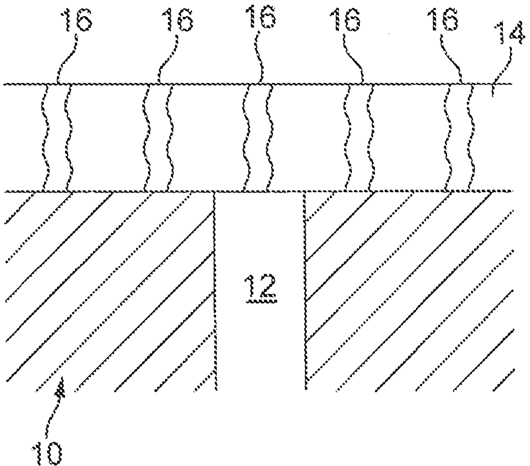

FIG. 2

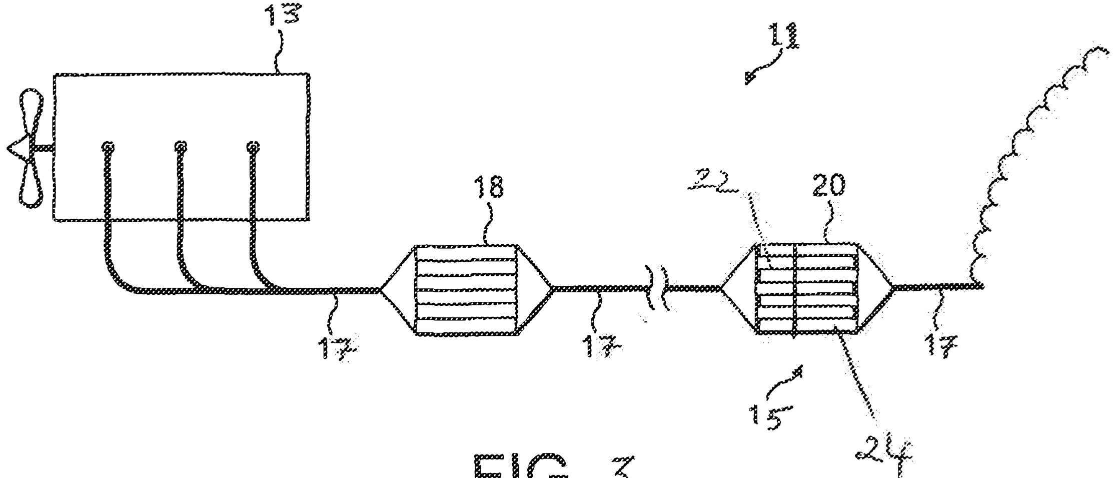

FIG. 3

POSITIVE IGNITION ENGINE AND EXHAUST SYSTEM COMPRISING CATALYSED ZONE-COATED FILTER SUBSTRATE

The present invention relates to a catalysed filter for filtering particulate matter from exhaust gas emitted from a positive ignition internal combustion engine.

Positive ignition engines cause combustion of a hydrocarbon and air mixture using spark ignition. Contrastingly, compression ignition engines cause combustion of a hydrocarbon by injecting the hydrocarbon into compressed air. Positive ignition engines can be fuelled by gasoline fuel, gasoline fuel blended with oxygenates including methanol and/or ethanol, liquid petroleum gas or compressed natural gas.

A three-way catalyst (TWC) typically contains one or more platinum group metals, particularly those selected from the group consisting of platinum, palladium and rhodium.

TWCs are intended to catalyse three simultaneous reactions: (i) oxidation of carbon monoxide to carbon dioxide, (ii) oxidation of unburned hydrocarbons to carbon dioxide and water; and (iii) reduction of nitrogen oxides to nitrogen and oxygen. These three reactions occur most efficiently when the TWC receives exhaust gas from an engine running at or about the stoichiometric point. As is well known in the art, the quantity of carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x) emitted when gasoline fuel is combusted in a positive ignition (e.g. spark-ignited) internal combustion engine is influenced predominantly by the air-to-fuel ratio in the combustion cylinder. An exhaust gas having a stoichiometrically balanced composition is one in which the concentrations of oxidising gases (NO_x and O_2) and reducing gases (HC and CO) are substantially matched. The air-to-fuel ratio that produces this stoichiometrically balanced exhaust gas composition is typically given as 14.7:1.

Theoretically, it should be possible to achieve complete conversion of O_2, NO_x, CO and HC in a stoichiometrically balanced exhaust gas composition to CO_2, H_2O and N_2 (and residual O_2) and this is the duty of the TWC. Ideally, therefore, the engine should be operated in such a way that the air-to-fuel ratio of the combustion mixture produces the stoichiometrically balanced exhaust gas composition.

A way of defining the compositional balance between oxidising gases and reducing gases of the exhaust gas is the lambda (λ) value of the exhaust gas, which can be defined according to equation (1) as:

Actual engine air-to-fuel ratio/Stoichiometric engine air-to-fuel ratio, (1)

wherein a lambda value of 1 represents a stoichiometrically balanced (or stoichiometric) exhaust gas composition, wherein a lambda value of >1 represents an excess of O_2 and NO_x and the composition is described as "lean" and wherein a lambda value of <1 represents an excess of HC and CO and the composition is described as "rich". It is also common in the art to refer to the air-to-fuel ratio at which the engine operates as "stoichiometric", "lean" or "rich", depending on the exhaust gas composition which the air-to-fuel ratio generates: hence stoichiometrically-operated gasoline engine or lean-burn gasoline engine.

It should be appreciated that the reduction of NO_x to N_2 using a TWC is less efficient when the exhaust gas composition is lean of stoichiometric. Equally, the TWC is less able to oxidise CO and HC when the exhaust gas composition is rich. The challenge, therefore, is to maintain the composition of the exhaust gas flowing into the TWC at as close to the stoichiometric composition as possible.

Of course, when the engine is in steady state it is relatively easy to ensure that the air-to-fuel ratio is stoichiometric. However, when the engine is used to propel a vehicle, the quantity of fuel required changes transiently depending upon the load demand placed on the engine by the driver. This makes controlling the air-to-fuel ratio so that a stoichiometric exhaust gas is generated for three-way conversion particularly difficult. In practice, the air-to-fuel ratio is controlled by an engine control unit, which receives information about the exhaust gas composition from an exhaust gas oxygen (EGO) (or lambda) sensor: a so-called closed loop feedback system. A feature of such a system is that the air-to-fuel ratio oscillates (or perturbates) between slightly rich of the stoichiometric (or control set) point and slightly lean, because there is a time lag associated with adjusting air-to-fuel ratio. This perturbation is characterised by the amplitude of the air-to-fuel ratio and the response frequency (Hz).

The active components in a typical TWC comprise one or both of platinum and palladium in combination with rhodium, or even palladium only (no rhodium), supported on a high surface area oxide, and an oxygen storage component.

When the exhaust gas composition is slightly rich of the set point, there is a need for a small amount of oxygen to consume the unreacted CO and HC, i.e. to make the reaction more stoichiometric. Conversely, when the exhaust gas goes slightly lean, the excess oxygen needs to be consumed. This was achieved by the development of the oxygen storage component that liberates or absorbs oxygen during the perturbations. The most commonly used oxygen storage component (OSC) in modern TWCs is cerium oxide (CeO_2) or a mixed oxide containing cerium, e.g. a Ce/Zr mixed oxide.

Ambient PM is divided by most authors into the following categories based on their aerodynamic diameter (the aerodynamic diameter is defined as the diameter of a 1 g/cm^3 density sphere of the same settling velocity in air as the measured particle):

(i) PM-10 - particles of an aerodynamic diameter of less than 10 μm;
(ii) Fine particles of diameters below 2.5 μm (PM-2.5);
(iii) Ultrafine particles of diameters below 0.1 μm (or 100 nm); and
(iv) Nanoparticles, characterised by diameters of less than 50 nm.

Since the mid-1990's, particle size distributions of particulates exhausted from internal combustion engines have received increasing attention due to possible adverse health effects of fine and ultrafine particles. Concentrations of PM-10 particulates in ambient air are regulated by law in the USA. A new, additional ambient air quality standard for PM-2.5 was introduced in the USA in 1997 as a result of health studies that indicated a strong correlation between human mortality and the concentration of fine particles below 2.5 μm.

Interest has now shifted towards nanoparticles generated by diesel and gasoline engines because they are understood to penetrate more deeply into human lungs than particulates of greater size and consequently they are believed to be more harmful than larger particles, extrapolated from the findings of studies into particulates in the 2.5-10.0 μm range.

Size distributions of diesel particulates have a well-established bimodal character that correspond to the particle nucleation and agglomeration mechanisms, with the corresponding particle types referred to as the nuclei mode and the accumulation mode respectively (see Figure 1). As can be seen from Figure 1, in the nuclei mode, diesel PM is composed of numerous small particles holding very little mass. Nearly all diesel particulates have sizes of significantly less than 1 μm, i.e. they comprise a mixture of fine, i.e. falling under the 1997 US law, ultrafine and nanoparticles.

Nuclei mode particles are believed to be composed mostly of volatile condensates (hydrocarbons, sulfuric acid, nitric acid etc.) and contain little solid material, such as ash and carbon. Accumulation mode particles are understood to comprise solids (carbon, metallic ash etc.) intermixed with condensates and adsorbed material (heavy hydrocarbons, sulfur species, nitrogen oxide derivatives etc.) Coarse mode particles are not believed to be generated in the diesel combustion process and may be formed through mechanisms such as deposition and subsequent re-entrainment of particulate material from the walls of an engine cylinder, exhaust system, or the particulate sampling system. The relationship between these modes is shown in Figure 1.

The composition of nucleating particles may change with engine operating conditions, environmental condition (particularly temperature and humidity), dilution and sampling system conditions. Laboratory work and theory have shown that most of the nuclei mode formation and growth occur in the low dilution ratio range. In this range, gas to particle conversion of volatile particle precursors, like heavy hydrocarbons and sulfuric acid, leads to simultaneous nucleation and growth of the nuclei mode and adsorption onto existing particles in the accumulation mode. Laboratory tests (see e.g. SAE 980525 and SAE 2001-01-0201) have shown that nuclei mode formation increases strongly with decreasing air dilution temperature but there is conflicting evidence on whether humidity has an influence.

Generally, low temperature, low dilution ratios, high humidity and long residence times favour nanoparticles formation and growth. Studies have shown that nanoparticles consist mainly of volatile material like heavy hydrocarbons and sulfuric acid with evidence of solid fraction only at very high loads.

Contrastingly, engine-out size distributions of gasoline particulates in steady state operation show a unimodal distribution with a peak of about 60-80nm (see e.g. Figure 4 in SAE 1999-01-3530). By comparison with diesel size distribution, gasoline PM is predominantly ultrafine with negligible accumulation and coarse mode.

Particulate collection of diesel particulates in a diesel particulate filter is based on the principle of separating gas-borne particulates from the gas phase using a porous barrier. Diesel filters can be defined as deep-bed filters and/or surface-type filters. In deep-bed filters, the mean pore size of filter media is bigger than the mean diameter of collected particles. The particles are deposited on the media through a combination of depth filtration mechanisms, including diffusional deposition (Brownian motion), inertial deposition (impaction) and flow-line interception (Brownian motion or inertia).

In surface-type filters, the pore diameter of the filter media is less than the diameter of the PM, so PM is separated by sieving. Separation is done by a build-up of collected diesel PM itself, which build-up is commonly referred to as “filtration cake” and the process as “cake filtration”.

It is understood that diesel particulate filters, such as ceramic wallflow monoliths, may work through a combination of depth and surface filtration: a filtration cake develops at higher soot loads when the depth filtration capacity is saturated and a particulate layer starts covering the filtration surface. Depth filtration is characterized by somewhat lower filtration efficiency and lower pressure drop than the cake filtration.

Other techniques suggested in the art for separating gasoline PM from the gas phase include vortex recovery.

Emission legislation in Europe from 1st September 2014 (Euro 6) requires control of the number of particles emitted from both diesel and gasoline (positive ignition) passenger cars. For gasoline EU light duty vehicles the allowable limits are: 1000mg/km carbon monoxide; 60mg/km nitrogen oxides (NO_X); 100mg/km total hydrocarbons (of which ≤ 68mg/km are non-methane hydrocarbons); and 4.5mg/km particulate matter ((PM) for direct injection engines only). The Euro 6 PM standard will be phased in over a number of years with the standard from the beginning of 2014 being set at 6.0 x 10^{12} per km (Euro 6) and the standard set from the beginning of 2017 being 6.0 x 10^{11} per km (Euro 6+).

It is understood that the US Federal LEV III standards have been set at 3mg/mile mass limit (currently 10mg/mile) over US FTP cycle from 2017-2021. The limit is then yet further tightened to 1mg/mile from 2025, although implementation of this lower standard may be brought forward to 2022.

The new Euro 6 (Euro 6 and Euro 6+) emission standard presents a number of challenging design problems for meeting gasoline emission standards. In particular, how to design a filter, or an exhaust system including a filter, for reducing the number of PM gasoline (positive ignition) emissions, yet at the same time meeting the emission standards for non-PM pollutants such as one or more of oxides of nitrogen (NO_X), carbon monoxide (CO) and unburned hydrocarbons (HC), all at an acceptable back pressure, e.g. as measured by maximum on-cycle backpressure on the EU drive cycle.

It is envisaged that a minimum of particle reduction for a three-way catalysed particulate filter to meet the Euro 6 PM number standard relative to an equivalent flowthrough catalyst is ≥50%. Additionally, while some backpressure increase for a three-way catalysed wallflow filter relative to an equivalent flowthrough catalyst is inevitable, in our experience peak backpressure over the MVEG-B drive cycle (average over three tests from “fresh”) for a majority of passenger vehicles should be limited to <200 mbar (<20,000 Pa), such as <180 mbar (<18,000 Pa), <150 mbar (<15,000 Pa) and preferably <120 mbar (<12,000 Pa) e.g. <100 mbar (<10,000 Pa).

WO 2011/077139 discloses a NOx trap comprising components comprising at least one platinum group metal, at least one NOx storage material and bulk ceria or a bulk cerium-containing mixed oxide deposited uniformly in a first layer on a honeycombed substrate monolith, the uniformly deposited components in the first layer having a first, upstream, zone having increased activity relative to a second, downstream zone for oxidising hydrocarbons and carbon monoxide, and a second, downstream, zone having increased activity to generate heat during a desulphation event, relative to the first, upstream, zone, wherein the second, downstream, zone comprises a dispersion of rare earth oxide, wherein the rare earth oxide loading in gin^{-3} in the second, downstream zone is greater than the rare earth oxide loading in the first, upstream zone.

WO 2011/110919 discloses a diesel engine aftertreatment system comprising a diesel engine having an exhaust manifold and a filter substrate in direct connection with the exhaust manifold without any intervening catalyst, wherein the filter substrate comprises on its inlet side an SCR catalyst incorporating a non-coking molecular sieve.

The new emission standards will force the use of filters for filtering particulate matter from exhaust gas emitted from positive ignition internal combustion engines. However, because the size of such particulate matter is much finer than particulate matter emitted from diesel engines, the design challenge is to filter particulate matter from positive ignition exhaust gas but at acceptable back pressure.

We have now discovered a way of catalysing a filter for use in the exhaust system of a vehicular positive ignition engine, thereby reducing the total volume of exhaust system components compared with separate filter and catalyst substrate components – which is important particularly on passenger vehicles where space can be restricted – but which has lower back pressure relative to a homogeneously coated catalysed filter, i.e. having coatings applied via inlet and outlet ends both at the same washcoat loading.

According to one aspect, the invention provides a positive ignition engine comprising an exhaust system, which exhaust system comprises a catalysed filter for filtering particulate matter from exhaust gas emitted from a positive ignition internal combustion engine, which filter comprising a ceramic porous filter substrate, which is a wall-flow filter having a total substrate length and having a plurality of inlet channels having inlet surfaces and a plurality of outlet channels having outlet surfaces, wherein the inlet surfaces of each inlet channel are separated from the outlet surfaces of each outlet channel by a ceramic wall of porous structure containing pores of a first mean pore size, wherein the wall-flow filter is coated with a washcoat composition which is a NOx absorber catalyst washcoat composition comprising at least one precious metal, wherein the porous structure of the washcoated ceramic wall of the wall-flow filter contains pores of a second mean pore size, wherein the second mean pore size is less than the first mean pore size, which NOx absorber catalyst washcoat being axially arranged on the wall-flow filter as a first zone comprising the inlet surfaces of a first substrate length less than the total substrate length and a second zone comprising the outlet surfaces of a second substrate length less than the total substrate length, wherein the sum of the substrate length in the first zone and the substrate length in the second zone is >110%, wherein:

(i) a washcoat loading in the first zone > second zone and the total precious metal loading is substantially the same in both the first zone and the second zone; or

(ii) both a washcoat loading and a total precious metal loading in the first zone > second zone,

and wherein the first zone is disposed upstream of the second zone.

For the total precious metal loading in feature (i), such feature is homogeneously applied between the inlet and outlet surfaces. So, since feature (i) defines only the washcoat loading, the total precious metal loading in the NOx absorber catalyst is substantially the same (homogeneous) in both the first zone and the second zone.

Mean pore size can be determined by mercury porosimetry.

NO_x absorber catalysts (NACs) are known e.g. from US patent no. 5,473,887 and are designed to adsorb nitrogen oxides (NO_x) from lean exhaust gas (lambda >1) and to desorb the NO_x when the oxygen concentration in the exhaust gas is decreased. Desorbed NO_x may be reduced to N_2 with a suitable reductant, e.g. gasoline fuel, promoted by a catalyst component, such as rhodium, of the NAC itself or located downstream of the NAC. In practice, control of oxygen concentration can be adjusted to a desired redox composition intermittently in response to a calculated remaining NO_x adsorption capacity of the NAC, e.g. richer than normal engine running operation (but still lean of stoichiometric or lambda = 1 composition), stoichiometric or rich of stoichiometric (lambda <1). The oxygen concentration can be adjusted by a number of means, e.g. throttling, injection of additional hydrocarbon fuel into an engine cylinder such as during the exhaust stroke or injecting hydrocarbon fuel directly into exhaust gas downstream of an engine manifold.

A typical NAC formulation includes a catalytic oxidation component, such as platinum, a significant quantity, i.e. substantially more than is required for use as a promoter such as a promoter in a TWC, of a NO_x-storage component, such as barium or ceria (CeO_2), and a reduction catalyst, e.g. rhodium. One mechanism commonly given for NO_x-storage from a lean exhaust gas for this formulation is:

$$NO + \frac{1}{2} O_2 \rightarrow NO_2 \qquad (2); \text{ and}$$

$$BaO + NO_2 + \frac{1}{2} O_2 \rightarrow Ba(NO_3)_2 \qquad (3),$$

wherein in reaction (2), the nitric oxide reacts with oxygen on active oxidation sites on the platinum to form NO_2. Reaction (3) involves adsorption of the NO_2 by the storage material in the form of an inorganic nitrate.

At lower oxygen concentrations and/or at elevated temperatures, the nitrate species become thermodynamically unstable and decompose, producing NO or NO_2 according to reaction (4) below. In the presence of a suitable reductant, these nitrogen oxides are subsequently reduced by carbon monoxide, hydrogen and hydrocarbons to N_2, which can take place over the reduction catalyst (see reaction (5)).

$$Ba(NO_3)_2 \rightarrow BaO + 2NO + {}^{3}/_{2} O_2 \text{ or } Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2} O_2 \qquad (4); \text{ and}$$

$$NO + CO \rightarrow \frac{1}{2} N_2 + CO_2 \qquad (5);$$

(Other reactions include $Ba(NO_3)_2 + 8H_2 \rightarrow BaO + 2NH_3 + 5H_2O$ followed by $NH_3 + NO_x \rightarrow N_2 + yH_2O$ or $2NH_3 + 2O_2 + CO \rightarrow N_2 + 3H_2O + CO_2$ etc.).

In the reactions of (2)-(5) above, the reactive barium species is given as the oxide. However, it is understood that in the presence of air most of the barium is in the form of the carbonate or possibly the hydroxide. The skilled person can adapt the above reaction schemes accordingly for species of barium other than the oxide and sequence of catalytic coatings in the exhaust stream and any other alkaline earth metals, alkali metals or lanthanides included for NOx absorption.

Modern NOx absorber catalysts coated on honeycomb flowthrough monolith substrates are typically arranged in layered arrangements. However, multiple layers applied on a filter substrate can create backpressure problems. It is highly preferable, therefore, if the NOx absorber catalyst for use in the present invention is a “single layer” NOx absorber catalyst. Particularly preferred “single layer” NOx absorber catalysts comprise a first component of rhodium supported on a ceria-zirconia mixed oxide or an optionally stabilised alumina (e.g.

stabilised with silica or lanthana or another rare earth element) in combination with second components which support platinum and/or palladium. The second components comprise platinum and/or palladium supported on an alumina-based high surface area support and a particulate “bulk” ceria (CeO_2) component, i.e. not a soluble ceria supported on a particulate support, but “bulk” ceria capable of supporting the Pt and/or Pd as such. The particulate ceria comprises a NOx absorber component and supports a lanthanide, an alkaline earth metal and/or an alkali metal, preferably barium, in addition to the platinum and/or palladium. The alumina-based high surface area support can be magnesium aluminate e.g. $MgAl_2O_4$, for example.

The preferred “single layer” NAC composition comprises a mixture of the rhodium and platinum and/or palladium support components. These components can be prepared separately, i.e. pre-formed prior to combining them in a mixture, or rhodium, platinum and palladium salts and the supports and other components can be combined and the rhodium, platinum and palladium components hydrolysed preferentially to deposit onto the desired support.

The filter is a wallflow filter comprising a ceramic porous filter substrate having a plurality of inlet channels and a plurality of outlet channels, wherein each inlet channel and each outlet channel is defined in part by a ceramic wall of porous structure, wherein each inlet channel is separated from an outlet channel by a ceramic wall of porous structure. This filter arrangement is also disclosed in SAE 810114, and reference can be made to this document for further details. Alternatively, the filter can be a foam, or a so-called partial filter, such as those disclosed in EP 1057519 or WO 01/080978. The ceramic porous filter substrate can be made from, e.g. silicon carbide, cordierite, aluminium nitride, silicon nitride, aluminium titanate, alumina, mullite e.g., acicular mullite (see e.g. WO 01/16050), pollucite, a thermet such as Al_2O_3/Fe, Al_2O_3/Ni or B_4C/Fe, or composites comprising segments of any two or more thereof.

It is a particular feature of the present invention that washcoat loadings used in the first, upstream zone can be higher than the previously regarded highest washcoat loadings, e.g. those disclosed in the Examples in WO 2010/097634. In a particular embodiment, the washcoat loading in the first zone is >1.60 g in^{-3} (>97.64 g/l), and in preferred embodiments the washcoat loading in the first zone is >2.4 g in^{-3} (>146.5 g/l). Preferably, however, the washcoat loading in the first zone is ≤ 3.0 g/in^{-3} (≤ 183.1 g/l).

In the catalysed filter according to the invention, the sum of the substrate length in the first zone and the substrate length in the second zone >110%, i.e. there is axial overlap, between the first zone on the inlet surface and the second zone on the outlet surface.

The length of axial overlap between inlet and outlet surface coatings ~~can be~~ is >10%, e.g. 10<30%, i.e. the sum of the substrate length in the first zone and the substrate length in the second zone >110%, e.g. 110<130%.

The substrate length in the first zone can be the same as or different from that of the second zone. So, where the first zone length is the same as the second zone length the porous substrate is coated in a ratio of 1:1 between the inlet surface and the outlet surface. However, in one embodiment, the substrate length in the first zone < the substrate length in the second zone.

In embodiments, the substrate length in the first zone < the substrate length in the second zone, e.g. <45%. In preferred embodiments, the substrate zone length in the first zone is <40%, e.g. <35% of the total substrate length.

In the catalysed filter of feature (ii), the total precious metal loading in the first zone > the total precious metal loading in the second zone. In particularly preferred embodiments, the total precious metal loading in the first zone is >50gft^{-3} (>1.77 g/l), but is preferably between 60-250gft^{-3} (2.1-8.8 g/l), and is typically from 70-150gft^{-3} (2.5-5.3 g/l). Total precious metal loadings in the second zone can be e.g. <50gft^{-3} (<1.77 g/l), e.g. <30gft^{-3} (<1.1 g/l) such as <20gft^{-3} (0.7 g/l).

In preferred embodiments, the first and second zones comprise a surface washcoat, wherein a washcoat layer substantially covers surface pores of the porous structure and the pores of the washcoated porous substrate are defined in part by spaces between the particles (interparticle pores) in the washcoat. Methods of making surface coated porous filter substrates include introducing a polymer, e.g. poly vinyl alcohol (PVA), into the porous structure, applying a washcoat to the porous filter substrate including the polymer and drying, then calcining the coated substrate to burn out the polymer. A schematic representation of the first embodiment is shown in Figure 2.

Methods of coating porous filter substrates are known to the skilled person and include, without limitation, the method disclosed in WO 99/47260, i.e. a method of coating a monolithic support, comprising the steps of (a) locating a containment means on top of a support, (b) dosing a pre-determined quantity of a liquid component into said containment means, either in the order (a) then (b) or (b) then (a), and (c) by applying pressure or vacuum, drawing said liquid component into at least a portion of the support, and retaining substantially all of said quantity within the support. Such process steps can be repeated from another end of the monolithic support following drying of the first coating with optional firing/calcination.

Alternatively, the method disclosed in WO 2011/080525 can be used, i.e. comprising the steps of: (i) holding a honeycomb monolith substrate substantially vertically; (ii) introducing a pre-determined volume of the liquid into the substrate via open ends of the channels at a lower end of the substrate; (iii) sealingly retaining the introduced liquid within the substrate; (iv) inverting the substrate containing the retained liquid; and (v) applying a vacuum to open ends of the channels of the substrate at the inverted, lower end of the substrate to draw the liquid along the channels of the substrate.

In this preferred embodiment, a mean interparticle pore size of the porous washcoat is 5.0nm to 5.0μm, such as 0.1-1.0μm.

As explained hereinabove, the NOx absorber catalyst washcoat composition for use in the first aspect of the present invention generally comprises solid particles. In embodiments, the mean size (D50) of the solid washcoat particles is in the range 1 to 40μm.

In further embodiments, the D90 of solid washcoat particles is in the range of from 0.1 to 20μm.

D50 and D90 measurements were obtained by Laser Diffraction Particle Size Analysis using a Malvern Mastersizer 2000 (RTM), which is a volume-based technique (i.e. D50 and D90 may also be referred to as Dv50 and Dv90 (or D(v,0.50) and D(v,0.90)) and applies a mathematical Mie theory model to determine a particle size distribution. Diluted washcoat samples were prepared by sonication in distilled water without surfactant for 30 seconds at 35 watts.

The porous substrate for use in the present invention is a ceramic wall flow filter made from e.g. cordierite, or silicon carbide or any of the other materials described hereinabove.

The cell density of diesel wallflow filters in practical use can be different from wallflow filters for use in the present invention in that the cell density of diesel wallflow filters is generally 300 cells per square inch (cpsi) (46.5 cells cm^{-2}) or less, e.g. 100 or 200 cpsi (15.5 to 31.0 g/l), so that the relatively larger diesel PM components can enter inlet channels of the filter without becoming impacted on the solid frontal area of the diesel particulate filter, thereby caking and fouling access to the open channels, whereas wallflow filters for use in the present invention can be up to 300 cpsi (46.5 cells cm^{-2}) or greater, such as 350 cpsi (54.3 cells cm^{-2}), 400 cpsi (62.0 cells cm^{-2}), 600 cpsi (93.0 cells cm^{-2}), 900 cpsi (139.5 cells cm^{-2}) or even 1200 cpsi (186.0 cells cm^{-2}).

An advantage of using higher cell densities is that the filter can have a reduced cross-section, e.g. diameter, than diesel particulate filters, which is a useful practical advantage that increases design options for locating exhaust systems on a vehicle.

It will be understood that the benefit of filters for use in the invention is substantially independent of the porosity of the uncoated porous substrate. Porosity is a measure of the percentage of void space in a porous substrate and is related to backpressure in an exhaust system: generally, the lower the porosity, the higher the backpressure. However, the porosity of filters for use in the present invention are typically >40% or >50% and porosities of 45-75% such as 50-65% or 55-60% can be used with advantage. The mean pore size of the washcoated porous substrate is important for filtration. So, it is possible to have a porous substrate of relatively high porosity that is a poor filter because the mean pore size is also relatively high.

In embodiments, the first mean pore size e.g. of surface pores of the porous structure of the porous filter substrate is from 8 to 45μm, for example 8 to 25μm, 10 to 20μm or 10 to 15μm. In particular embodiments, the first mean pore size is >18μm such as from 15 to 45μm, 20 to 45μm e.g. 20 to 30μm, or 25 to 45μm.

In a preferred embodiment, the exhaust system of the positive ignition engine comprises a flow through monolith substrate comprising a three-way catalyst composition disposed upstream of the catalysed filter. The engine is configured intermittently to run rich, e.g. to regenerate the NO_x absorption capacity of the NO_x absorber catalyst, and rich exhaust gas contacting the TWC and/or NO_x absorber can generate ammonia *in situ* for use in reducing NO_x on a downstream honeycomb substrate comprising a SCR catalyst, preferably any of the following SCR catalysts. Ammonia can be generated in situ e.g. during rich regeneration of a NAC disposed upstream of the filter or by contacting a TWC with engine-derived rich exhaust gas (see the alternatives to reactions (4) and (5) hereinabove).

SCR catalysts can be selected from the group consisting of at least one of Cu, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, such as Fe, supported on a refractory oxide or molecular sieve. Suitable refractory oxides include Al_2O_3, TiO_2, CeO_2, SiO_2, ZrO_2 and mixed oxides containing two or more thereof. The non-zeolite catalyst can also include tungsten oxide, e.g. $V_2O_5/WO_3/TiO_2$, $WOx/CeZrO_2$, WOx/ZrO_2 or $Fe/WOx/ZrO_2$.

In particular embodiments, an SCR catalyst washcoat comprises at least one molecular sieve, such as an aluminosilicate zeolite or a SAPO. The at least one molecular sieve can be a small, a medium or a large pore molecular sieve, for example. By “small pore molecular sieve” herein we mean molecular sieves containing a maximum ring size of 8, such as CHA; by “medium pore molecular sieve” herein we mean a molecular sieve containing a maximum ring size of 10, such as ZSM-5; and by “large pore molecular sieve” herein we mean a molecular sieve having a maximum ring size of 12, such as beta. Small pore molecular sieves are potentially advantageous for use in SCR catalysts – see for example WO 2008/132452.

Particular molecular sieves with application as SCR catalysts in the present invention are synthetic aluminosilicate zeolite molecular sieves selected from the group consisting of AEI, ZSM-5, ZSM-20, ERI including ZSM-34, mordenite, ferrierite, BEA including Beta, Y, CHA, LEV including Nu-3, MCM-22 and EU-1, preferably AEI or CHA, and having a silica-to-alumina ratio of about 10 to about 50, such as about 15 to about 40.

Where the reductant is a nitrogenous reductant (so-called “NH_3-SCR”), metals of particular interest are selected from the group consisting of Ce, Fe and Cu.

Suitable nitrogenous reductants include ammonia. Alternatively, the nitrogenous reductant or a precursor thereof can be injected directly into the exhaust gas. Suitable precursors include ammonium formate, urea and ammonium carbamate. Decomposition of the precursor to ammonia and other by-products can be by hydrothermal or catalytic hydrolysis.

In a further preferred embodiment, a honeycomb substrate comprising a SCR catalyst (preferably any of the preferred SCR catalysts disclosed hereinabove) is disposed downstream of the filter. Intermittent rich running of the engine, e.g. to regenerate the NO_x absorption capacity of the NO_x absorber catalyst, can generate ammonia *in situ* on the TWC or NO_x absorber for use in reducing NO_x on a downstream SCR catalyst.

That is, the exhaust system of the positive ignition engine according to the invention can comprise a series of monolith substrates disposed in a flow direction from upstream to downstream as follows: (i) NOx absorber catalyst on a filter substrate according to the first aspect of the invention followed by a honeycomb substrate comprising a SCR catalyst, wherein the engine is configured intermittently to run rich, thereby to generate ammonia *in situ* on the NOx absorber catalyst component; and (ii) as (i) except in that a TWC on a flow through monolith substrate is disposed upstream of the NOx absorber catalyst on the filter according to the first aspect of the invention, wherein ammonia may be generated *in situ* on both the TWC component and the NOx absorber catalyst component.

Exhaust systems comprising SCR catalyst require nitrogenous reductant to promote the NOx reduction reaction, i.e. to be effective, nitrogenous reductant should be present in exhaust gas flowing into the SCR catalyst. As mentioned in the preceding paragraphs, in certain preferred embodiments, such nitrogenous reductant e.g. ammonia, is generated *in situ* by contacting a TWC and/or a NOx absorber catalyst component with a rich exhaust gas. However, alternatively or in addition to *in situ* ammonia generation, in further preferred embodiments, the exhaust system comprises an injector for injecting a nitrogenous reductant precursor such as urea into exhaust gas upstream of the SCR catalyst component. Such injector is fluidly linked to a source of such nitrogenous reductant precursor, e.g. a tank thereof, and valve-controlled dosing of the precursor into the exhaust stream is regulated by suitably programmed engine management means and closed loop or open loop feedback provided by sensors monitoring relevant exhaust gas composition.

Positive ignition internal combustion engines, such as spark ignition internal combustion engines, for use in this aspect of the invention can be fuelled by gasoline fuel, gasoline fuel blended with oxygenates including methanol and/or ethanol, liquid petroleum gas or compressed natural gas.

According to a second aspect, the invention provides a method of simultaneously converting oxides of nitrogen and particulate matter in the exhaust gas of a positive ignition internal combustion engine, which method comprising the step of contacting the gas with a catalysed filter comprising a ceramic porous filter substrate, which is a wall-flow filter having a total substrate length and having a plurality of inlet channels having inlet surfaces and a plurality of outlet channels having outlet surfaces, wherein the inlet surfaces of each inlet channel are separated from the outlet surfaces of each outlet channel by a ceramic wall of porous structure containing pores of a first mean pore size, wherein the wall-flow filter is coated with a washcoat composition which is a NOx absorber catalyst washcoat composition comprising at least one precious metal, wherein the porous structure of the washcoated ceramic wall of the wall-flow filter contains pores of a second mean pore size, wherein the second mean pore size is less than the first mean pore size, which NOx absorber catalyst washcoat being axially arranged on the wall-flow filter as a first zone comprising the inlet surfaces of a first substrate length less than the total substrate length and a second zone comprising the outlet surfaces of a second substrate length less than the total substrate length, wherein the sum of the substrate length in the first zone and the substrate length in the second zone is >110% , wherein:

(i) a washcoat loading in the first zone > second zone and the total precious metal loading is substantially the same in both the first zone and the second zone; or

(ii) both a washcoat loading and a total precious metal loading in the first zone > second zone,

wherein the gas contacts the first zone prior to contacting the second zone.

In order that the invention may be more fully understood, reference is made to the accompanying drawings wherein:

Figure 1 is a graph showing the size distributions of PM in the exhaust gas of a diesel engine. For comparison, a gasoline size distribution is shown at Figure 4 of SAE 1999-01-3530;

Figure 2 is a schematic drawing of an embodiment of a washcoated porous filter substrate according to the invention; and

Figure 3 is a schematic drawing of an embodiment of an exhaust system for the purposes of comparative illustration only.

Figure 2 shows a cross-section through a porous filter substrate 10 comprising a surface pore 12. Figure 2 shows an embodiment, featuring a porous surface washcoat layer 14 comprised of solid washcoat particles, the spaces between which particles define pores (interparticle pores). It can be seen that the washcoat layer 14 substantially covers the pore 12 of the porous structure and that a mean pore size of the interparticle pores 16 is less than the mean pore size 12 of the porous filter substrate 10.

Figure 3 shows an apparatus 11 for the purposes of comparative illustration only and comprising a vehicular positive ignition engine 13 and an exhaust system 15 therefor. Exhaust system 15 comprises a conduit 17 linking catalytic aftertreatment components, namely a Pd-Rh-based TWC coated onto an inert cordierite flowthrough substrate 18 disposed close to the exhaust manifold of the engine (the so-called close coupled position). Downstream of the close-coupled catalyst 18 in turn is a zoned CuCHA SCR catalyst coated onto a cordierite wall-flow filter 20 having a total length and comprising inlet channels coated to a length of one third of the total length measured from an upstream or inlet end of the wall-flow filter with a washcoat loading of 2.8 gin^{-3} (170.1 g/l), which coating defining a first zone 22. The outlet channels are coated with a CuCHA SCR catalyst coated on two thirds of the total length of the wall-flow filter measured from the downstream or outlet end of the wall-flow filter with a washcoat loading of 1.0 gin^{-3} (61.0 g/l), which coating defining a second zone 24. Engine management means (not shown) is run intermittently rich, i.e. in "rich spike"–type mode, thereby to contact the upstream TWC with enriched exhaust gas and to generate ammonia and other reformed nitrogenous reductant species *in situ* and to promote NOx conversion on the downstream SCR catalyst.

In order that the invention may be more fully understood the following Examples are provided by way of illustration only. The Examples are not according to the invention. However, all three Examples illustrate the principle of loading a filter with a similar quantity of catalyst compared to reference catalysts at reduced backpressure. Example 2 is relevant to a NOx absorber catalyst embodiment, wherein the first upstream zone has a higher platinum group metal loading than the second downstream zone with improvements in both hydrocarbon light off temperature, which is also an important aspect of NOx absorber catalyst activity, and backpressure. The washcoat loadings quoted in the Examples were obtained using the method disclosed in WO 2011/080525.

Example 1 (not according to the invention)

Two cordierite wall-flow filters of dimensions 4.66 x 5.5 inches (11.8 x 14.0 cm), 300 cells per square inch (46.5 cells cm^{-2}), wall thickness 12 thousandths of an inch (0.305 mm) and having a mean pore size of 20 μm and a porosity of 65% were each coated with a TWC composition in a different configuration from the other. In each case, the TWC composition was milled to a d90 <17 μm) so that the coating when applied would be expected preferentially to locate more at the surface of a wallflow filter wall ("on-wall").

A first filter (referred to in Table 1 as having a "Homogeneous" washcoat loading) was coated in channels intended for the inlet side of the filter with a TWC washcoat zone extending for a targeted 33.3% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising a precious metal loading of 85 g/ft^3 (3.0 g/l) (80Pd:5Rh) and at a washcoat loading of 2.4 g/in^3 (146.5 g/l). The outlet channels were coated to a length of 66.6% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising a precious metal loading of 18 g/ft^3 (0.64 g/l) (16Pd:2Rh) at a washcoat loading also of 2.4 g/in^3 (146.5 g/l). X-ray imaging was used to ensure that an overlap occurred in the longitudinal plane between the inlet channel zone and the outlet channel zone. So, the washcoat loading was homogeneous between the first and second zones, but the platinum group metal loading in the first zone > second zone.

A second filter (referred to in Table 1 as having a "Zoned" washcoat loading) was coated in the inlet channels with a TWC washcoat zone extending for a targeted 33.33% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising a precious metal loading of 85 g/ft^3 (3.0 g/l) (80Pd:5Rh) and at a washcoat loading of 2.8 g/in^3 (170.9 g/l). The outlet channels were coated to a length of 66.66% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising a precious metal loading of 18 g/ft^3 (0.64 g/l) (16Pd:2Rh) at a washcoat loading of 1.0 g/in^3 (61.0 g/l). X-ray imaging was used to ensure that an overlap occurred in the longitudinal plane between the inlet channel zone and the outlet channel zone. So, both the washcoat loading and the platinum group metal loading in the first zone > second zone.

The total precious metal content of the first and second filters was identical.

Each filter was hydrothermally oven-aged at 1100°C for 4 hours and installed in a close-coupled position on a Euro 5 passenger car with a 2.0L direct injection gasoline engine. Each filter was evaluated over a minimum of three MVEG-B drive cycles, measuring the reduction in particle number emissions relative to a reference catalyst. The reference catalyst was a TWC coated homogeneously onto a 600 cells per square inch (93.0 cells cm^{-2}) cordierite flowthrough substrate monolith having the same dimensions as the first and second filters and at a washcoat loading of $3gin^{-3}$ (183.1 g/l) and a precious metal loading of $33gft^{-3}$ (1.17 g/l) (30Pd:3Rh). The backpressure differential was determined between sensors mounted upstream and downstream of the filter (or reference catalyst).

In Europe, since the year 2000 (Euro 3 emission standard) emissions are tested over the New European Driving Cycle (NEDC). This consists of four repeats of the previous ECE 15 driving cycle plus one Extra Urban Driving Cycle (EUDC) with no 40 second warm-up period before beginning emission sampling. This modified cold start test is also referred to as the "MVEG-B" drive cycle. All emissions are expressed in g/km.

The Euro 5/6 implementing legislation introduces a new PM mass emission measurement method developed by the UN/ECE Particulate Measurement Programme (PMP) which adjusts the PM mass emission limits to account for differences in results using old and the new methods. The Euro 5/6 legislation also introduces a particle number emission limit (PMP method), in addition to the mass-based limits.

The results of the tests are shown in Table 1, from which it can be seen that the filter washcoated in the zoned configuration shows improved back pressure and has good (though moderately lower) levels of particle number reduction relative to the homogeneously washcoated filter. Despite the moderate reduction in lower particle number reduction, the second filter would still meet the full Euro 6+ (2017) standard limit.

Sample filter properties	**Washcoat type**	**% PN reduction** vs. **flow through reference**	**Average BP (mbar) (kPa) on 70 kph cruise of MVEG-B drive cycle**	**Peak BP (mbar) (kPa) during any one MVEG-B drive cycle**
20 µm, 65%	Homogeneous	85	17.6 (1.76 kPa)	82.1 (8.21 kPa)
20 µm, 65%	Zoned	81	12.2 (1.22 kPa)	59.5 (5.95 kPa)

Table 1. Effect of washcoat zoning on particle number reduction and backpressure (BP)

<u>Example 2 (not according to the invention)</u>

Two cordierite wall-flow filters of dimensions 4.66 x 4.5 inches (11.8 x 11.4 cm), 300 cells per square inch (46.5 cells cm^{-2}), wall thickness 12 thousandths of an inch (0.305 mm), mean pore size of 20 µm and a porosity of 65% were each coated with a TWC composition in a different configuration from the other. In each case, the TWC composition was milled to a d90 <17 µm) so that the coating when applied would be expected preferentially to locate more at the surface of a wallflow filter wall ("on-wall").

A third filter (referred to in Table 2 as having a "Homogeneous" platinum group metal loading (Comparative Example)) was coated in channels intended for the inlet side of the filter and outlet side of the filter with a TWC washcoat zone extending for a targeted 50% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising a precious metal loading of $60gft^{-3}$ (2.1 g/l) (57Pd:3Rh) and at a washcoat loading of 2.4 g/in^3 (146.5 g/l).

A fourth filter (referred to in Table 2 as having a "Zoned" PGM loading) was coated in channels intended for the inlet side of the filter with a TWC washcoat zone extending for a targeted 50% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising $100g/ft^3$ (3.5 g/l) precious metal (97Pd:3Rh) at a washcoat loading of 2.4 g/in^3 (146.5 g/l); and the outlet channels were coated with a TWC washcoat zone extending for a targeted 50% of the total length of the filter substrate measured from the open channel ends with a washcoat comprising 20 g/ft^{-3} (0.71 g/l) precious metal (17Pd:3Rh), also at a washcoat loading of 2.4 g/in^{3} (146.5 g/l). .

The total precious metal content of the third and fourth filters was identical.

Each filter was hydrothermally oven-aged at 1100°C for 4 hours and installed in a close-coupled position on a Euro 5 passenger car with a 1.4L direct injection gasoline engine. Each filter was evaluated over a minimum of three MVEG-B drive cycles, measuring the reduction in particle number emissions relative to a reference catalyst. Peak backpressure (BP) was also evaluated in the same way as described in Example 1.

Hydrocarbon light-off temperature (the temperature at which the catalyst catalyses the conversion of hydrocarbons in the feed gas at 50% efficiency or greater) was evaluated on a separate engine mounted in a laboratory test cell. This engine was a 2.0 litre turbo charged direct injection gasoline engine. The exhaust gas temperature was carefully regulated and increased from 250-450°C over a given period of time through the use of a combination of a temperature heat sink and increasing throttle position, during which time the conversion efficiency of the catalyst was measured and reported.

The results of zone coating the precious metal in the filter substrate are shown in Table 2, from which it can be seen that – as could be expected with identical washcoat loadings between the two filters – the % particle number reduction vs. the flow through reference catalyst (homogeneous 60gft^{-3} (2.1 g/l) precious metal content (57Pd:3Rh) at 3 gin^{-3} (183.1 g/l) homogeneous washcoat loading on a 600 cells per square inch (93.0 cells cm^{-2}) cordierite monolith substrate having the same dimensions as the third and fourth filters) are identical. However, the hydrocarbon light-off is higher for the Homogenous PGM configuration relative to the Zoned configuration. This can be attributed to the higher concentration of PGM on the inlet side.

Sample filter properties	**PGM zoning**	**HC light-off temperature (°C)**	**% PN reduction** vs. **flow through reference**	**Peak BP (mbar) (kPa) during any one MVEG-B drive cycle**
20 µm, 65%	Homogeneous	391	73	37.5 (3.75 kPa)
20 µm, 65%	Zoned	379	73	35.8 (3.58 kPa)

Table 2. Effect of PGM zoning on light-off temperature

CLAIMS:

1. A positive ignition engine comprising an exhaust system, which exhaust system comprises a catalysed filter for filtering particulate matter from exhaust gas emitted from a positive ignition internal combustion engine, which filter comprising a ceramic porous filter substrate, which is a wall-flow filter having a total substrate length and having a plurality of inlet channels having inlet surfaces and a plurality of outlet channels having outlet surfaces, wherein the inlet surfaces of each inlet channel are separated from the outlet surfaces of each outlet channel by a ceramic wall of porous structure containing pores of a first mean pore size, wherein the wall-flow filter is coated with a washcoat composition which is a NOx absorber catalyst washcoat composition comprising at least one precious metal, wherein the porous structure of the washcoated ceramic wall of the wall-flow filter contains pores of a second mean pore size, wherein the second mean pore size is less than the first mean pore size, which NOx absorber catalyst washcoat being axially arranged on the wall-flow filter as a first zone comprising the inlet surfaces of a first substrate length less than the total substrate length and a second zone comprising the outlet surfaces of a second substrate length less than the total substrate length, wherein the sum of the substrate length in the first zone and the substrate length in the second zone is > 110%, wherein:

(i) a washcoat loading in the first zone > second zone and the total precious metal loading is substantially the same in both the first zone and the second zone; or

(ii) both a washcoat loading and a total precious metal loading in the first zone > second zone

and wherein the first zone is disposed upstream of the second zone.

2. A positive ignition engine according to claim 1, wherein the NOx absorber catalyst comprises a mixture of (i) rhodium supported on a ceria-zirconia mixed oxide or an optionally stabilised alumina; and (ii) platinum and/or palladium supported on an alumina-based high surface area support and ceria, wherein an alkaline earth metal, an alkali metal or a lanthanide is supported on the ceria.

3. A positive ignition engine according to claim 1 or 2, wherein the washcoat loading in the first zone is >1.60 gin^{-3} (>97.6 g/l).

4. A positive ignition engine according to any preceding claim, wherein a substrate length in the first zone is different from that of the second zone.

5. A positive ignition engine according to claim 4, wherein the substrate length in the first zone is < the substrate length in the second zone.

6. A positive ignition engine according to claim 5, wherein the substrate zone length in the first zone is <45% of the total substrate length.

7. A positive ignition engine according to feature (ii) in any preceding claim, wherein the total precious metal loading in the first zone of the NOx absorber catalyst is >50 gft^{-3} (>1.77 g/l).

8. A positive ignition engine according to any preceding claim, comprising a surface washcoat, wherein a washcoat layer substantially covers surface pores of the porous structure and the pores of the washcoated porous substrate are defined in part by spaces between the particles (interparticle pores) in the washcoat.

9. A positive ignition engine according to any preceding claim, wherein the mean size of the solid washcoat particles is in the range 1 to 40μm.

10. A positive ignition engine according to claim 8 or 9, wherein a D90 of solid washcoat particles is in the range 0.1 to 20μm.

11. A positive ignition engine according to any preceding claim, wherein the uncoated porous substrate has a porosity of >40%.

12. A positive ignition engine according to any preceding claim, wherein a first mean pore size of the porous structure of the porous substrate is from 8 to 45μm.

13. A positive ignition engine according to any preceding claim, wherein the exhaust system comprises a flow through monolith substrate comprising a three-way catalyst composition disposed upstream of the catalysed filter.

14. A method of simultaneously converting oxides of nitrogen and particulate matter in the exhaust gas of a positive ignition internal combustion engine, which method comprising the step of contacting the gas with a catalysed filter comprising a ceramic porous filter substrate, which is a wall-flow filter having a total substrate length and having a plurality of inlet channels having inlet surfaces and a plurality of outlet channels having outlet surfaces, wherein the inlet surfaces of each inlet channel are separated from the outlet surfaces of each outlet channel by a ceramic wall of porous structure containing pores of a first mean pore size, wherein the wall-flow filter is coated with a washcoat composition which is a NOx absorber catalyst washcoat composition comprising at least one precious metal, wherein the porous structure of the washcoated ceramic wall of the wall-flow filter contains pores of a second mean pore size, wherein the second mean pore size is less than the first mean pore size, which NOx absorber catalyst washcoat being axially arranged on the wall-flow filter as a first zone comprising the inlet surfaces of a first substrate length less than the total substrate length and a second zone comprising the outlet surfaces of a second substrate length less than the total substrate length, wherein the sum of the substrate length in the first zone and the substrate length in the second zone is > 110%, wherein:

(i) a washcoat loading in the first zone > second zone and the total precious metal loading is substantially the same in both the first zone and the second zone; or

(ii) both a washcoat loading and a total precious metal loading in the first zone > second zone,

wherein the gas contacts the first zone prior to contacting the second zone.