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(71) Applicant *(for all designated States except US)*: JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2–4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: TWIGG, Martyn, Vincent [GB/GB]; 108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB). WISHART, Ian, Carmichael [GB/GB]; Bagpuize House, Baker Street, Aston Tirrold, Oxfordshire OX11 9DD (GB).

(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

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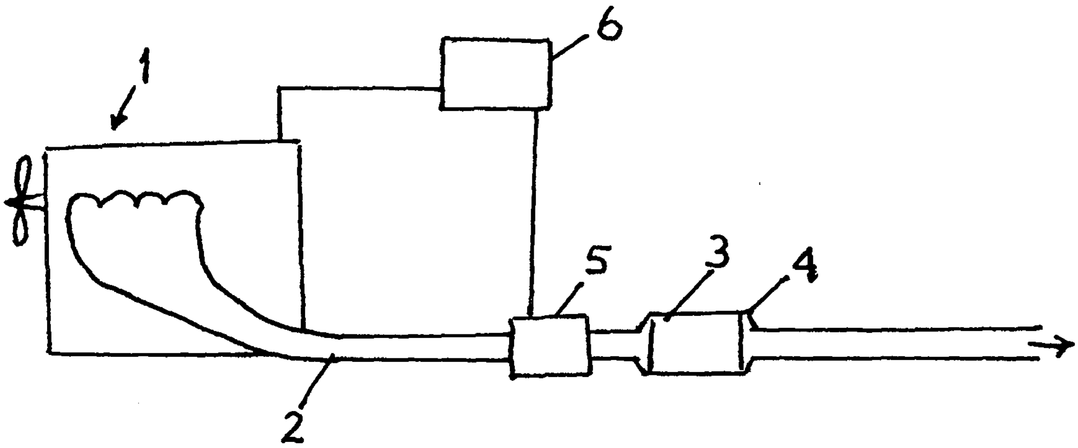

(57) Abstract

A system for purifying exhaust gases from a diesel or like engine (1) comprises a filter (3) and a plasma generator (5). The plasma generator converts NO and/or N_2 to NO_2 and/or generates ozone, which is found to be particularly effective at causing low temperature combustion of soot trapped on the filter.

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SYSTEM AND METHOD FOR PURIFYING EXHAUST GASES

This invention concerns the purification of exhaust gases, especially the purification of such gases from diesel and other "lean-burn" engines.

Diesel engines are in widespread use in all types of vehicles, stationary power sources and naval and commercial shipping. They are very fuel-efficient, but because of their combustion characteristics generate particulate matter (soot, often called "PM") on which a variety of organic substances may be absorbed, including unburnt hydrocarbons (HC) and sulphuric acid produced by oxidation of sulphur dioxide derived from sulphur species present in the fuel or in lubricants. Other engines, such as gasoline direct injection ("GDI"), can also produce significant quantities of PM, and we consider that the need for removing such PM will soon be expressed in legislation. Nonetheless, the invention may be applied to combustion processes generally, as well as potentially to chemical process stacks/exhausts, and to combustion engines operating at $\lambda=1$ or greater, or lean-burn engines operating at stoichiometric or rich in order to regenerate some exhaust gas aftertreatment device. For simplicity, however, we concentrate on diesel engines hereinafter.

In order to meet various regulations concerning the level of pollutants, it has become commonplace to fit vehicles with an oxidation or three-way catalyst, which only achieves partial removal of PM. The removal of particulates is generally achieved by using some form of filter or trap, which may be cleaned or regenerated intermittently. It has been suggested to include a catalyst in the fuel to the engine, and as well as platinum group metals ("PGMs"), iron, copper or cerium compounds have been suggested. A particulate trap may be catalysed to lower the soot combustion temperature, and some form of external heating, for example electric heating of the trap or of air fed thereto, may be used to initiate soot combustion.

A particularly successful soot trap is marketed by Johnson Matthey PLC as the "CRT" ("Continuously Regenerating Technology") and is described in US Patent 4 902 487. This system uses a conversion of NO in the exhaust gas to NO_2, which was discovered to be much more effective at typical low diesel exhaust gas temperatures in the combustion of soot than air or any other exhaust gas component. Thus, NO_2 is typically effective to combust PM at about 250°C, whereas oxygen is effective at about 650°C.

It has been suggested to use a plasma generator for exhaust gas purification (see for example GB 2,274,412 and 2 270 013, UK Atomic Energy Authority). Although it was probably not previously recognised in connection with exhaust gas treatment, such a system produces considerable quantities of NO_2. Systems such as previously described do not include any filter or trap in combination with a plasma generator, but we believe that this may be a particularly effective system for treating diesel and similar lean-burn exhaust gases.

Accordingly, the present invention provides a system for the treatment of such exhaust gases, comprising a plasma generator effective to convert at least a portion of NO and/or nitrogen in the exhaust gases to NO_2 and/or to generate ozone and a filter effective to trap a desired proportion of soot from the exhaust gases, whereby said trapped soot is combusted by reaction with NO_2 and/or ozone, at a markedly lower temperature than required by O_2.

We believe, although we do not wish to be bound by any theory, that in the present invention NO_2 may be generated not only by oxidation of NO in the exhaust gases, but also by oxidation of nitrogen to yield NO, which is itself converted to NO_2. In the latter case, there is no reliance upon the quantities of NOx leaving the engine. It is also believed that the present invention is especially valuable in that it is not badly affected by the presence of sulphur in the fuel or in lubricants, which can poison conventional catalysts.

The invention further provides a method of reducing emissions from exhaust gases from diesel and like engines, comprising trapping soot on a filter and continuously or intermittently combusting the soot by reaction with NO_2 and/or ozone produced by a plasma generator, preferably using a plasma treatment of at least a portion of the exhaust gases.

The plasma generator may be any suitable type producing a non-thermal plasma, and may be enhanced by electromagnetic radiation. Suitable plasma generators include high voltage (e.g. 20kV or more) alternating current, preferably pulsed, generators, suitably using two dielectric plates positioned in the gas flow, and piezoelectric devices such as piezoceramic transformers. It may be positioned to treat all or a portion of the exhaust gases upstream of the filter, or may be fitted downstream of the filter to treat all or a portion of the filtered exhaust gas, with recirculation of plasma-treated gases to the filter. In one embodiment of the present invention, a pre-determined proportion of the exhaust gases is treated by the plasma to cause substantially all of the NO present to be converted into NO_2, and the resulting gases blended with untreated exhaust gases, thus resulting in a blend of NO and NO_2, which according to some studies, may be more effective for the purposes of the present invention than a gas containing substantially only NO_2 in admixture with other exhaust gas components.

The filter used may be a woven or knitted wire filter, a gas-permeable metal or ceramic foamed mass or a wall flow filter of generally known type (honeycomb monolith). For certain vehicles, especially light cars or vans, it may be necessary or desirable, to use a filter design which collects only 80% or so by weight of the total soot particulates and preferably incorporates a by-pass and/or pressure relief valve. The filter may be partially or completely catalysed if desired. A catalysed trap may improve the aggregate removal of pollutants..

A modification of the present invention incorporates a means for removing NOx downstream of the filter and plasma generator. Such means may be a NOx trap, which technology is available to the skilled person, and generally includes one or more alkali earth metal compounds, especially calcium oxide or barium oxide, or alkali metal, carried on a metal or ceramic honeycomb-type support. The NOx trap is desirably used in combination with a lean-NOx catalyst. Another means for removing NOx is Selective Catalytic Reduction ("SCR"), which is well established for stationary power sources and is receiving increasing attention for vehicular applications. Such a modified system can be effective to meet all current and known future emission control regulations for diesel and like engines.

The plasma generator may be controlled and actuated by an engine management unit, or other microprocessor control unit, to operate intermittently according to certain engine operating conditions (speed, load *etc*) which have been pre-determined to generate more soot. Alternatively, the plasma generator may operate during all operational conditions of the engine, which system has the benefit of simplicity, but this may be undesirable if the engine is in an operating condition in which significant quantities of NOx are generated, or during regeneration of a NOx trap.

The present invention, at least in its most preferred embodiments, in addition to being particularly effective at controlling emissions, permits the engine designers to design and tune the engine for power and/or fuel efficiency, rather than being forced to make compromises in engine design to minimise the generation of NOx and particulates. This can be a significant advantage for commercial vehicles, but allows flexibility in design for all engines and types of vehicles.

A further variant of the present invention is to feed a reductant, which term includes hydrocarbon fuel, e.g. diesel fuel, ammonia, ammonia precursors, hydrogen etc. into the exhaust gases either upstream or downstream of the plasma generator.

The present invention is illustrated with reference to the accompanying drawing, which is a schematic diagram of a system according to the invention.

A diesel engine is shown at 1, and has an exhaust system, 2. Conventional silencer boxes and ancilliary equipment are not shown. A wall flow filter, 3, retained within a metal box, 4, is mounted in the exhaust system. Mounted close upstream to the filter, is a plasma generator, 5, which is operated according to signals from the engine management unit, 6.

Testing of the described system is continuing, but early indications are that substantially all soot particles trapped on the filter are removed continuously, although there are variations in soot build up and removal rates. NO_2 and ozone have been detected in the exhaust gases after the plasma generator, with substantially lower levels after the filter.

The following Examples illustrate features of the present invention.

EXAMPLE 1

The non-thermal plasma discharge generator used comprised a ceramic tube 10 cm long and 5 cm external diameter in which a bed of pelleted material of suitable dielectric constant was held between two circular stainless steel mesh electrodes. The mesh aperture size was about 0.5 mm. Typically the pellets were of size about 3 mm, and occupied a length of 1-3 cm in the ceramic tube. The packed volume was about 12-36 cm^3. One electrode was earthed via a large spring that maintained a physical pressure on the bed of pellets. The other electrode was fixed and connected to the 'live' side of a power supply capable of providing an adjustable AC voltage at 50 Hz up to 10 kV and powers of up to 1 kW.

A gas mixture designed to approximate key features of exhaust gas from a diesel engine containing nitric oxide (300 ppm), propene (300 ppm), oxygen (12%), and water vapour (about 1%) with the balance being helium was passed through the plasma generator at a flow rate of 250 ml min^{-1}. A mass spectrometer was used to determine and quantify the composition of gas exiting the generator. When operating at ambient temperature with a voltage of about 3 kV applied across the electrodes destruction of propene was almost 100%, and a large quantity of carbon dioxide was formed. However, the amount of carbon dioxide was only about 35% of that expected for complete combustion. Traces of formaldehyde were detected but carbon monoxide probably accounted for most of the other oxidation products. However, its quantification was complicated by traces of nitrogen having a similar mass number.

Nitric oxide was also completely removed when the potential was applied to the electrodes, and substantial levels of nitrogen dioxide (mass 46) were detected in the exit gas. The amount of nitrogen dioxide detected typically corresponded to about 55% of the amount of the original nitric oxide and depended on the nature of the pellets. With alumina pellets higher surface area material (eg 200 m^2 g^{-1}) gave higher conversions than low surface area material (eg 5 m^2 g^{-1}). Alumina pellets coated with a thin layer of barium titanate or lead titanate gave higher conversions than just pure alumina pellets. Increasing the voltage applied across the electrodes also increased conversion of nitric oxide to nitrogen dioxide. These experiments demonstrate nitric oxide is oxidised to nitrogen dioxide by passage through a non-thermal plasma even when hydrocarbon is present.

EXAMPLE 2

A cordierite wallflow filter (5.66 inch diameter, 6.0 inch long) having 100 cells $inch^{-2}$ and 17/1000 inch thick walls was located in the exhaust pipe of a four cylinder 1.9 litre direct injection turbo charged Diesel engine that ran on fuel containing 350 ppm sulphur. The engine was operated at 1200 rpm with half load for 10 hours. The filter was then removed from the exhaust pipe and ground to a powder that was pressed into small granules (250-350 μm). A sample of these sooty black granules (0.05 g) was placed in a stainless steel tube (6 mm diameter) and held in place by two small loose plugs of quartz wool. The tube was connected to the exit of the plasma generator of Example 1, and the gas was heated to temperatures in the range of 150-300°C by electrical heating tape before passing over the sample containing Diesel soot. Analysis of the gas once it had passed over the soot containing sample was achieved by a mass spectrometer. Increasing the temperature of the gas passing over the sample resulted in increasing amounts of carbon dioxide being formed, and increasing amounts of nitric oxide in the gas after the sample. After maintaining the sample temperature at about 240°C for an hour the discharged granules had only a light grey colouration indicating that most of the soot had been removed by exposure to the plasma treated gas. This experiment shows that gas containing nitric oxide that has been oxidised in a non-thermal plasma generator oxidises Diesel soot at temperatures above about 150°C, and so such a device could be used to keep a Diesel particulate filter free of excess soot by continuously combusting soot, even at relatively low temperatures.

It will be appreciated that many variations may be made to the system as particularly described, without departing from the present inventive concept. In particular, the skilled person will appreciate that Example 2 above illustrates a practical method for removing soot from a filter even at the low temperatures met with many modern engine designs, particularly when operating at idle or under low load. This is a valuable contribution to the art.

CLAIMS

1. A system for the treatment of exhaust gases, for example from diesel and like internal combustion engines, comprising a plasma generator effective to generate NO_2 from NO and/or nitrogen contained in the exhaust gases, and/or to generate ozone, and a filter effective to trap a desired proportion of particulate matter from the exhaust gases, whereby trapped soot is combusted by reaction with NO_2 and/or with ozone.

2. A system according to claim 1, wherein the plasma generator is located upstream of the filter and all or a portion of the exhaust gases from the engine are passed therethrough.

3. A system according to claim 1, wherein the plasma generator is located downstream of the filter and all or a portion of the plasma-treated and filtered exhaust gases are recirculated to the upstream side of the filter.

4. A system according to any one of the preceding claims, wherein a proportion of the exhaust gases are plasma treated and blended with untreated exhaust gases to create a desired blend of NO and NO_2.

5. A system according to any one of the preceding claims, comprising also means for removing or reducing NOx mounted downstream of the filter and plasma generator.

6. A system according to claim 5, wherein the means for removing or reducing NOx comprises a NOx trap.

7. A system according to claim 5, wherein the means for removing or reducing NOx comprises SCR.

8. A system according to any one of the preceding claims, wherein the plasma generator comprises a piezoelectric device.

9. A system according to any one of the preceding claims, wherein the plasma generator is controlled by an engine management unit or other microprocessor control unit, to operate intermittently according to pre-determined engine operating conditions.

10. A method of reducing emissions from exhaust gases from diesel and like engines, comprising trapping soot on a filter and continuously or intermittently combusting the soot by reaction with NO_2 and/or ozone produced by a plasma generator.

11. A method according to claim 9, wherein all, or a portion of, the exhaust gases are passed through the plasma generator and contacted with trapped soot.

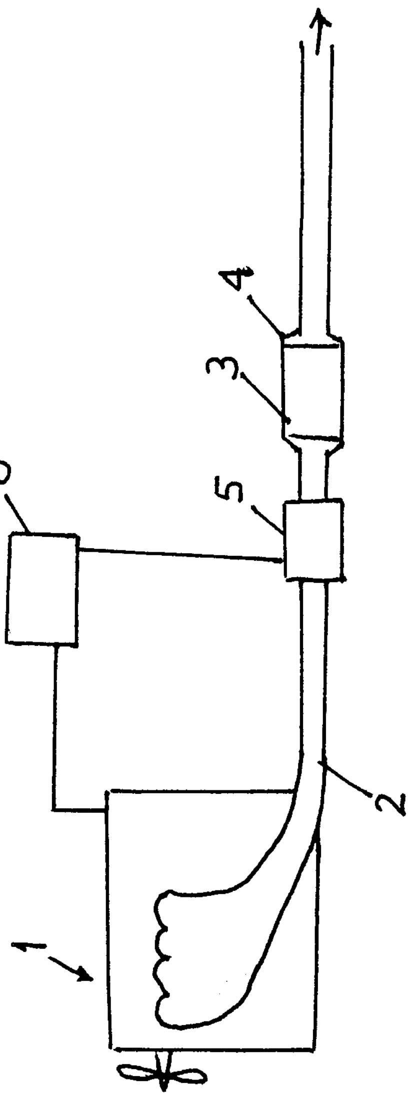

Fig 1

INTERNATIONAL SEARCH REPORT

Inte[illegible]onal Application No
PCT/GB 99/03102

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/32 B01D53/94 F01N3/08 F01N3/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D F01N

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 98 09699 A (UNIV CALIFORNIA) 12 March 1998 (1998-03-12) page 18, line 23 - line 28 page 23, line 19 - line 25 page 24, line 15 - line 22 --- -/--	1-11

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	AKIRA MIZUNO ET AL.: "Reactive Absorption of NOx Using Wet Discharge Plasma Reactor" IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS, vol. 31, no. 6, December 1995 (1995-12), pages 1463-1468, XP000550029 New York page 1463, left-hand column	1-11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No

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