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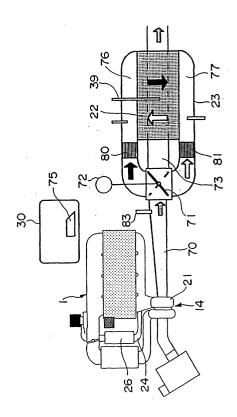
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(54) Exhaust gas purifier for internal combustion engine

(57) In an exhaust gas purifier provided with a collecting material for collecting particulate matters contained in exhaust discharged from an internal combustion engine, by restraining generation of ash, a pressure loss of exhaust due to clog the collecting material is prevented. In an exhaust gas purifier for an internal combustion engine which is provided with a collecting material for collecting particulate matters contained in exhaust discharged from the internal combustion engine, ash traps (80, 81) for absorbing phosphorous (P) in exhaust gas are provided upstream of a particulate filter (22). The ash traps (80, 81) load with basic metal. The formation of ash due to combine Phosphorous (P) with calcium (Ca) and to be concentrated in the particulate filter (22) is restrained.

Fig. 2



Description

BACKGROUND OF THE INVENTION

1. Technical Filed

[0001] The present invention relates to an exhaust gas purifier for removing particulate matters in exhaust gas discharged from an internal combustion engine.

2. Description of the Related Art

[0002] In an internal combustion engine that is mounted on an automobile or the like, it is required to purify harmful gas components such as nitrogen oxide (NOx) and hydrocarbon (HC) contained in exhaust gas to improve exhaust emission. In particular, in the case of a diesel engine, it is important to decrease so-called particulate matters (PM) such as soot and SOF (Soluble Organic Fraction) in addition to nitrogen oxide and hydrocarbon.

[0003] In order to cope with such a requirement, "an exhaust gas purifier for an internal combustion engine" as described in Japanese Patent No. 2722987 was proposed in the past. The exhaust gas purifier for an internal combustion engine described in the patent is provided with a particulate filter for collecting particulate matters in exhaust gas in an exhaust passageway of an internal combustion engine and has an NOx absorbent, which absorbs NOx in exhaust gas when an air-fuel ratio of the exhaust gas is lean and emits and reduces absorbed NOx when an oxygen concentration in exhaust gas is low and an absorbent exists, disposed in a position where the NOx absorbent can transfer heat to and from the particulate filter.

[0004] With such a configuration, the exhaust gas purifier for an internal combustion engine causes temperature of the particulate filter to rise utilizing heat generated when a reducer burns on the NOx absorbent to thereby burn and remove the particulate matters collected in the particulate filter.

[0005] On the other hand, when a particulate filter is used, an exhaust channel in the particulate filter is blocked by concentration of a compound called ash and thus a pressure loss of exhaust gas increases.

[0006] Although a mechanism for generating ash has not been clarified, it is presumed that various additives and impurities contained in fuel and lubricating oil of an internal combustion engine combine with each other in a combustion chamber of the internal combustion engine or on the particulate filter, to thereby form various compounds which concentrate on the particulate filter to generate ash.

[0007] For example, components such as sulfur (S), phosphorous (P), calcium (Ca) and magnesium (Mg) are contained in fuel and lubricating oil of an internal combustion engine, and components contained in blowby gas (lubricating oil) and components contained in air-

fuel mixture combine in a combustion chamber to generate compounds such as calcium sulfate (CaSO₄), calcium phosphate (Ca₃(PO₄)₂) and magnesium sulfate (MgSO₄), which are collected on a particulate filter together with particulate matters (PM) to concentrate as ash

[0008] In addition, since sulfur (S) has a characteristic that it is easily absorbed in soot, sulfur (S) absorbed in a particulate filter together with soot combines with calcium (Ca) and magnesium (Mg) in exhaust gas to generate compounds such as calcium sulfate (CaSO₄) and magnesium sulfate (MgSO₄), which concentrate as ash. [0009] In order to cope with this problem, Japanese Patent Application Laid-open No. 2001-12229 discloses an exhaust gas purifier for an internal combustion engine, which is provided with a collecting material for collecting particulate matters, the collecting material having loaded therewith a metal having an electronegativity equal to or lower than that of a predetermined component contained in fuel and/or lubricating oil of an internal combustion engine.

[0010] In this way, the collecting material is loaded with the metal having an electronegativity equal to or lower than a predetermined component contained in lubricant, preferably a metal having an electronegativity lower than that of the predetermined component and strong ionization tendency. As a result, since a component to be combined combines with the metal rather than with the predetermined component, formation of the ash is inhibited.

[0011] However, it has been found that, even if the collecting material is used, it is difficult to prevent plugging of a particulate filter by calcium phosphate $(Ca_3(PO_4)_2)$ as an ash component.

[0012] This is because, although phosphorous P and sulfur S do not usually combine with each other, calcium Ca that most easily combines with phosphorous P is contained as calcium sulfate (CaSO₄) as described above, whereby phosphorous P and sulfur S concentrate in the particulate filter to be collected therein. Then, plugging by calcium phosphate (Ca₃(PO₄)₂) occurs in the particulate filter.

[0013] In particular, when a vehicle continuously runs in a region of that temperature of exhaust gas becomes high, a needle-like crystal of calcium phosphate (Ca $_3$ (PO $_4$) $_2$) is formed on a surface of a particulate filter loading with a noble metal such as platinum (Pt) and having a catalytic function, whereby a space is generated between purified matters and the noble metal, and the catalytic function may be down by half or lifetime of a catalyst may be shorten.

SUMMARY OF THE INVENTION

[0014] The present invention has been devised in view of the above-mentioned circumstance and it is an object of the present invention to provide a technology capable of inhibiting generation of ash, in particular,

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generation of ash due to calcium phosphate $(Ca_3 (PO_4)_2)$, in an exhaust gas purifier provided with a collecting material for collecting particulate matters contained in exhaust gas that is discharged from an internal combustion engine.

[0015] The present invention adopts the following measures in order to solve the above problem.

[0016] That is, the exhaust gas purifier for an internal combustion engine according to the present invention is characterized in that, in an exhaust gas purifier for an internal combustion engine which is provided with a collecting material for collecting particulate matters contained in exhaust discharged from the internal combustion engine, an ash trap for absorbing phosphorous (P) in exhaust gas is provided upstream of the collecting material.

[0017] In the exhaust gas purifier configured as described above, the collecting material collects particulate matters contained in exhaust gas discharged from the internal combustion engine. The term of the collecting material here may be, for example, an ordinary DPF (Diesel Particulate Filter) for collecting particulate matters or a DPF loaded with a catalytic substance such as a NOx absorbent.

[0018] In addition, it is likely that components originally contained in fuel and/or lubricating oil of the internal combustion engine exist in the exhaust gas. Therefore, there are possibility that a given components of those components may combine with another component (hereinafter referred to as a combined component) on the collecting material to form ash. However, if the ash trap is provided upstream of the collecting material, since the phosphor (P) is absorbed by the ash trap, formation of ash can be restrained by the collecting material provided downstream of the ash trap.

[0019] This ash trap may be loaded with a basic metal with strong ionization tendency. In this way, it becomes possible to steadily absorb phosphorous (P) in the form of calcium phosphate $(Ca_3(PO_4)_2)$ or the like.

[0020] The term of the basic metal here means a metal having an electronegativity such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), francium (Fr), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra) and lanthanum (La), preferably a metal having an electronegativity lower than that of the predetermined component and having strong ionization tendency. Since phosphorous P steadily combines with these metals, formation of ash by calcium phosphate $(Ca_3(PO_4)_2)$ in the collecting material downstream of the ash trap is inhibited.

[0021] In addition, it is preferable to load the collecting material with a metal having an electronegativity equal to or lower than a predetermined component contained in fuel or lubricant oil of the internal combustion engine. In this way, it is possible to restrain the concentration on the collecting material as ash consisting of a compound such as calcium sulfate $(CaSO_4)$ and magnesium sulfate $(MgSO_4)$ which combined sulfur (S) with calcium

(Ca) and magnesium (Mg) in exhaust gas.

[0022] Further, since it is likely that the compounds of the metal loaded on the collecting material and the predetermined component such as sulfur concentrate on the collecting material in the same manner as the ash does, it is preferable to select the metal to be loaded such that these compounds are decomposed or removed under the same conditions as purifying conditions of particulate matters.

[0023] In addition, the ash trap may be imparted with an oxidation performance. If the oxidation performance is imparted, since concentration of calcium phosphate (Ca₃(PO₄)₂) that is formed by phosphorous and calcium combining with each other is facilitated, it becomes easy to trap phosphorous here.

[0024] According to the present invention, in order to prevent phosphorous in exhaust gas from being combined with calcium and being concentrated on a collecting material to form ash, an ash trap loaded with a basic metal having an electronegativity that would facilitate combining thereof with phosphorous is provided in a pre-stage of this collecting material so that phosphor is absorbed by this ash trap. Thus, it is possible to inhibit ash from being formed by calcium phosphate $(Ca_3(PO_4)_2)$ in the collecting material.

[0025] Other objects and features of the present invention will be apparent from the following descriptions taken in conjunction with the accompanying drawings, in which like reference characters designate the same or similar parts throughout the figures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] In the accompanying drawings:

Fig. 1 illustrates a schematic configuration of an internal combustion engine to which an exhaust gas purifier in accordance with the present invention is applied:

Fig. 2 illustrates an exhaust gas purifier mounted with a particulate filter;

Fig. 3A is an image view showing a state in which particulates deposit on a filter base material;

Fig. 3B is an image view showing a state in which particulates are disturbed by forward flow and back flow of exhaust gas;

Fig. 4A is a front view of a particulate filter;

Fig. 4B is a side sectional view of the particulate filter; and

Figs. 5A and 5B are a conceptual view showing an oxidation action of particulates.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] An exhaust gas purifier in accordance with the present invention will be described based on the drawings. In this description, an embodiment in which the ex-

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haust gas purifier in accordance with the present invention is applied to a diesel engine for a vehicle will be described.

[0028] Referring to Fig. 1, reference numeral 1 denotes an engine main body, 2 denotes a cylinder block, 3 denotes a cylinder head, 4 denotes a piston, 5 denotes a combustion chamber, 6 denotes an electrically-controlled fuel injection valve, 7 denotes an intake valve, 8 denotes an intake port, 9 denotes an exhaust valve and 10 denotes an exhaust port. The intake port 8 is coupled to a surge tank 12 via an intake branch pipe 11 and the surge tank 12 is coupled to a compressor 15 of an exhaust turbocharger 14 via an intake duct 13. A throttle valve 17 driven by a step motor 16 is disposed in the intake duct 13 and a cooling device 18 for cooling intake air flowing in the intake duct 13 is disposed around the intake duct 13. In an example shown in Fig. 1, engine cooling water is guided into the cooling device 18 and the intake air is cooled by the engine cooling water.

[0029] On the other hand, the exhaust port 10 is coupled to an exhaust turbine 21 of the exhaust turbocharger 14 via an exhaust manifold 19 and an exhaust pipe 20. The outlet of the exhaust turbine 21 is coupled to an exhaust gas purifier having a casing 23 incorporating a particulate filter 22.

[0030] The exhaust manifold 19 and the surge tank 12 are coupled with each other via an exhaust gas recirculation (hereinafter referred to as EGR) passageway 24 and an electrically-controlled EGR control valve 25 is disposed in the EGR passageway 24. In addition, a cooling device 26 for cooling EGR gas flowing in the EGR passageway 24 is disposed around the EGR passageway 24. In the example shown in Fig. 1, the engine cooling water is guided into the cooling device 26 and the EGR gas is cooled by the engine cooling water.

[0031] On the other hand, each fuel injection valve 6 is coupled to a fuel reservoir, a so-called common-rail 27, via a fuel supply pipe 6a. Fuel is supplied into the common-rail 27 from an electrically-controlled fuel pump 28 that can change a discharge amount. The fuel supplied to the common-rail 27 is supplied to the fuel injection valve 6 via each fuel supply pipe 6a. A fuel pressure sensor 29 for detecting a fuel pressure in the common-rail 27 is attached to the common-rail 27. A fuel discharge amount by the fuel pump 28 is controlled such that the fuel pressure in the common-rail 27 becomes equal to a target fuel pressure, based on an output signal of the fuel pressure sensor 29.

[0032] An electronic control unit 30 consists of a digital computer and is provided with an ROM (Read Only Memory) 32, an RAM (Random Access Memory) 33, a CPU (microprocessor) 34, an input port 35 and an output port 36, which are connected with each other by a bidirectional bus 31. An output signal of the fuel pressure sensor 29 is inputted in an input port 35 via an corresponding AD converter 37. In addition, a floor temperature sensor 39 for detecting a floor temperature of the particulate filter 22 is attached to the particulate filter 22.

An output signal of the floor temperature sensor 39 is inputted in the input port 35 via the corresponding AD converter 37.

[0033] In addition, a load sensor 41 for generating an output voltage proportional to an amount of stepping L on an accelerator pedal 40 is connected to the accelerator pedal 40 and an output voltage of the load sensor 41 is inputted in the input port 35 via the corresponding converter 37. Moreover, a crank angle sensor 42 for generating an output pulse each time a crank shaft rotates by, for example, 30°, is connected to the input port 35. On the other hand, the output port 36 is connected to the fuel injection valve 6, the step motor 16 for driving a throttle valve, the EGR control valve 25, the fuel pump 28 and an actuator 72 discussed below via a corresponding driving circuit 38.

<Structure of the exhaust gas purifier>

[0034] As shown in Figs. 1 and 2, in the exhaust gas purifier, an exhaust pipe 70 is connected to the outlet of the exhaust turbine 21. The exhaust gas purifier is provided with a first exhaust passageway 76 and a second exhaust passageway 77 which branch from the exhaust pipe 70 to be respectively connected to one side and the other side of the filter 22 in the casing 23 incorporating the particulate filter 22. Moreover, the exhaust gas purifier is provided with a bypass passageway 73 for discharging exhaust gas directly without passing the exhaust gas through the particulate filter 22 from the branch point of the first exhaust passageway 76 and the second exhaust passageway 77.

[0035] In addition, an exhaust switching valve 71 is provided in the branch point of the first exhaust passageway 76 and the second exhaust passageway 77. The exhaust switching valve 71 is driven by the actuator 72 and alternately switches between first flow (forward flow) in which the first exhaust passageway 76 is selected to flow exhaust gas from one side of the filter 22 and second flow (back flow) in which the second exhaust passageway 77 is selected to flow exhaust gas from the other side of the filter 22.

[0036] Further, ash traps 80 and 81 are respectively provided in a pre-stage of the particulate filter 22 in the first exhaust passageway 76 and the second exhaust passageway 77. The ash traps 80 and 81 are loaded with basic metal with strong ionization tendency and phosphorous (P) in exhaust gas is absorbed by the basic metal.

[0037] The basic metal in this context includes, for example, one of lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), francium (Fr), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra) and lanthanum (La) or a combination of two or more of these.

[0038] Moreover, a fuel adding nozzle 83 as reducer adding means for injecting fuel into exhaust gas flowing into the filter 22 is provided in the first exhaust passage-

way 77. The fuel-adding nozzle 83 is controlled by controlling means that is realized on the CPU 34 of the electronic control unit 30.

[0039] Here, the casing 23 for accommodating the filter 22 is disposed in a position right above the exhaust pipe 70 forming the bypass passageway 73. The first exhaust passageway 76 and the second exhaust passageway 77 branching from the exhaust pipe 70 are connected to both sides of the casing 23. In addition, provided that a passing direction of exhaust gas is a length direction, in the filter 22 in the casing 23 a length in a width direction perpendicular to the length direction is longer than a length in the length direction. With such a configuration, a space for mounting the exhaust gas purifier consisting of the casing 23 enclosing the filter 22 can be reduced.

[0040] On the other hand, the actuator 72 is driven to be controlled by controlling means 75 realized on the CPU 34 of the electronic control unit 30 and is driven by a control signal from the output port 36. In addition, the actuator 72 is driven by a negative pressure that is formed with driving of the internal combustion engine. The actuator 72 controls a valve body into a position for selecting the first exhaust passageway 76 (forward flow position) when a negative pressure is not applied, controls the valve body into a neutral position when a first negative pressure is applied and controls the valve body into a position for selecting the second exhaust passageway 77 (back flow position) when a second negative pressure stronger than the first negative pressure is applied.

[0041] When the valve body is in the forward flow position indicated by broken lines of Fig. 2, the exhaust switching valve 71 connects the exhaust pipe 70 to the first exhaust passageway 76 and, at the same time, connects the second exhaust passageway 77 to the bypass passageway 73. Therefore, exhaust gas flows in the order of the exhaust pipe 70, the first exhaust passageway 76, the filter 22, the second exhaust passageway 77 and the bypass passageway 73 to be released to the atmosphere.

[0042] When the valve body in the back flow position indicated by a solid line of Fig. 2, the exhaust switching valve 71 connects the exhaust pipe 70 to the second exhaust passageway 77 and, at the same time, connects the first exhaust passageway 76 to the bypass passageway 73. Therefore, exhaust gas flows in the order of exhaust pipe 70, the second exhaust passageway 77, the filter 22, the first exhaust passageway 76 and the bypass passageway 73 to be released to the atmosphere

[0043] When the valve body is in the neutral position that is in parallel with the axis of the exhaust pipe 70 as indicated by alternate long and short dash lines of Fig. 2, the exhaust switching valve 71 connects the exhaust pipe 70 directly to the bypass passageway 73. Therefore, exhaust gas flows from the exhaust pipe 70 to the bypass passageway 73 without passing through the fil-

ter 22 to be released to the atmosphere.

[0044] Switching between the forward flow and the back flow is repeated by the switching of the valve body, whereby particulates such as soot move around in the base material of the filter 22. Therefore, oxidation of the particulates is facilitated and, as a result, purification of the particulates can be performed efficiently.

[0045] Fig 3A is an image view in the case where exhaust gas is flown through the filter 22 only in one direction. In this case, since particulates accumulate only on one side of the filter and do not move, particles not only causes increase of a pressure loss of exhaust gas but also hinders purification of the particulates.

[0046] Fig. 3B is an image view in the case where exhaust gas is flown through the filter 22 in the both directions. In this case, since particulates are disturbed in the forward flow direction and the back flow direction on both the sides of the filter, the particulates move around on both the side of the filter 22 or in the base material, whereby oxidation of the particulates can be facilitated utilizing active sites existing all over the filter base material and accumulation of the particulates on the filter 22 can be further decreased. Thus, increase of a pressure loss of exhaust gas can be avoided.

<Structure of the ash trap>

[0047] Although a shape and a structure of each of the ash traps 80 and 81 are not specifically limited as long as they can collect particulates, if possible, the ash traps with a large surface area is preferable.

[0048] For example, the ash traps 80 and 81 may be a so-called "wall flow type" which forms a honeycomb structure, in which a porous substance is used as a base material, and in which are alternately arranged, in a honeycomb form, first flow paths with end portions on their upstream sides opened and end portions on their downstream sides blocked, and second flow paths with end portions on their upstream sides blocked and end portions on their downstream sides opened. The first flow paths become exhaust gas inflow passageways with their downstream ends blocked by plugs and the second flow paths become exhaust gas outflow passageways with their upstream ends blocked by plugs. These passageways are alternately disposed through thin partitions.

[0049] Phosphorous (P) in exhaust gas is absorbed in the ash traps 80 and 81. In practice, phosphorous (P) combines with calcium (Ca) and concentrates in the ash traps 80 and 81 in the form of calcium phosphate (Ca $_3$ (PO $_4$) $_2$). Therefore, in the particulates filter 22 provided downstream of the ash traps 80 and 81, the formation of ash by calcium phosphate (Ca $_3$ (PO $_4$) $_2$) which is combined phosphorous (P) with calcium (Ca) is restrained. **[0050]** Alternatively, the ash traps 80 and 81 may be provided in a pre-stage of a switching flow path, that is, in a pre-stage of the exhaust switching valve 71. Further, phosphorous (P) in exhaust gas can be trapped doubly

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by providing the ash traps also in a pre-stage of the exhaust turbocharger 14. That is, the ash traps exist in both a position close to an exhaust manifold where temperature is high and a position in the first exhaust passageway 76 or the second exhaust passageway 77. Therefore, since they can absorb phosphorous (P) respectively in areas with extremely large temperature difference from each other, trap efficiency is improved.

<Structure of the filter>

[0051] Fig. 4 shows a structure of the particulate filter 22. Fig. 4A shows a front view of the particulate filter 22 and Fig. 4B shows a side sectional view of the particulate filter 22. As shown in Figs. 4A and 4B, the particulate filter 22 forms a honeycomb structure and is of a socalled "wall flow type" provided with a plurality of exhaust flow passageways 50 and 51 extending in parallel with each other. These exhaust flow passageways are constituted by the exhaust gas inflow passageways 50 with their downstream ends blocked by plugs 52 and the exhaust gas outflow passageways 51 with their upstream ends blocked by plugs 53. Further, portions with hatching in Fig. 4A indicate the plugs 53. Therefore, the exhaust gas inflow passageways 50 and the exhaust gas outflow passageways 51 are alternately disposed through thin partitions 54. In other words, the exhaust gas inflow passageways 50 and the exhaust gas outflow passageways 51 are arranged such that each exhaust gas inflow passageway 50 is surrounded by four exhaust gas outflow passageways 51 and each exhaust gas outflow passageway 51 is surrounded by four exhaust gas inflow passageways 50.

[0052] The particulate filter 22 is formed of a porous material such as a cordierite. Therefore, exhaust gas that has flown into the exhaust gas inflow passageways 50 flows out into the adjoining exhaust gas outflow passageways 51 by passing through the partitions 54 around them as indicated by arrows in Fig. 4B.

[0053] In the embodiment in accordance with the present invention, layers of a carrier made of, for example, aluminum are formed on circumferential wall surfaces of each exhaust gas inflow passageway 50 and each exhaust gas outflow passageway 51, that is, on both side surfaces of each partition 54 and on internal wall surfaces of pores in the partition 54. Loaded on this carrier are a noble metal catalyst and an active oxygen releaser for taking in and holding oxygen when excessive oxygen exists around it and releasing the held oxygen in the form of active oxygen when an oxygen concentration falls around it.

[0054] Platinum (Pt) can be used as the noble metal catalyst. In addition, the active oxygen releaser can be constituted by at least one metal selected out of: an alkali metal such as potassium (K), sodium (Na), lithium (Li), cesium (Cs) and rubidium (Rb); an alkali-earth metal such as barium (Ba), calcium (Ca) and strontium (Sr); a rare-earth such as lanthanum (La) and yttrium (Y); and

a transition metal such as cerium (Ce).

[0055] Further, a valence number of the transition metal (oxygen absorbing agent) such as cerium (Ce) changes according to an oxygen concentration. Thus, active oxygen is released at a large amount by repeating change in an oxygen concentration as follows.

CeO2 (lean)
$$\leftarrow \rightarrow$$
 CeO3 (rich)

[0056] In addition, it is preferable to use an alkali metal or an alkali-earth metal having higher ionization tendency than that of calcium (Ca), that is, potassium (K), lithium (Li), cesium (Cs), rubidium (Rb), barium (Ba) and strontium (Sr), as the active oxygen releaser.

[0057] In this embodiment, description will be made with the case in which platinum (Pt) is loaded as the noble metal catalyst and potassium (K) is loaded as the active oxygen releaser, on a carrier formed of aluminum or the like as an example.

<Continuous oxidation treatment of particulates by the filter>

[0058] Next, an action for removing particulates in exhaust gas by the particulate filter 22 will be described. Further, the action for removing particulates is also performed in the same mechanism even when using other alkali metals, alkali-earth metals, rare-earth or transition metals as the active oxygen releaser.

[0059] In a compression ignition internal combustion engine as shown in Fig. 1, combustion is performed under a condition of excessive air ratio and, therefore, exhaust gas contains a large amount of excessive air. That is, an air-fuel ratio of the exhaust gas is lean in the compression ignition internal combustion engine as shown in Fig. 1. In addition, since nitrogen monoxide (NO) is generated in the combustion chamber 5, nitrogen monoxide (NO) is contained in the exhaust gas. Further, sulfur (S) is contained in fuel and the sulfur (S) reacts with oxygen in the combustion chamber 5 to be sulfur dioxide (SO₂). Therefore, sulfur dioxide (SO₂) is contained in the exhaust gas. Therefore, the exhaust gas containing excessive oxygen, nitrogen monoxide (NO) and sulfur dioxide (SO₂) flows into the exhaust gas inflow passageway 50.

[0060] Figs. 5A and 5B schematically show enlarged views of the inner circumference surface of the exhaust gas inflow passageway 50 and a surface of a carrier layer formed on the pore inner wall surface within the partition 54. Further, in Figs. 5A and 5B, reference numeral 60 denotes particles of platinum (Pt) and 61 denotes an active oxygen releaser containing potassium (K).

[0061] As described above, since a large amount of excessive oxygen is contained in exhaust gas, when the exhaust gas flows into the exhaust gas inflow passageways 50 of the particulate filter 22, the oxygen (O_2) deposits on the surface of the platinum (Pt) in the form of

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 ${\rm O_2}$ - or ${\rm O_2}$ - as shown in Fig. 5A. On the other hand, nitrogen monoxide (NO) in the exhaust gas reacts with the ${\rm O_2}$ - or ${\rm O_2}$ - on the surface of the platinum (Pt) to become nitrogen dioxide ${\rm NO_2}$ (2NO+O₂ \rightarrow 2NO₂). Subsequently, a part of the generated nitrogen dioxide (NO₂) is absorbed in the active oxygen releaser 61 while being oxidized on the platinum (Pt) and diffuses in the active oxygen releaser 61 in the form of nitrogen oxide ion (NO₃-) as shown in Fig. 5A while combining with potassium (K) . A part of the nitrogen oxide ion (NO₃-) generates potassium nitrate (KNO₃).

[0062] On the other hand, sulfur dioxide (SO_2) is also contained in the exhaust gas as described above and this sulfur dioxide (SO_2) is also absorbed in the active oxygen releaser 61 by the same mechanism as that for absorbing nitrogen dioxide (NO). That is, oxygen (O_2) deposits on the surface of the platinum (Pt) in the form of O_2 - or O^2 - as described above and the SO_2 in the exhaust gas reacts with the O_2 - or O^2 - on the surface of the platinum (Pt) to become (SO_3).

[0063] Subsequently, a part of the generated (SO_3) is absorbed in the active oxygen releaser 61 while being further oxidized on the platinum (Pt) and diffuses in the active oxygen releaser 61 in the form of sulfate oxide ion (SO_4^{2-}) while combining with potassium K to generate potassium sulfate (K_2SO_4). In this way, potassium nitrate (KNO_3) and potassium sulfate (K_2SO_4) are generated in the active oxygen releaser 61.

[0064] On the other hand, particulates consisting mainly of carbon C are generated in the combustion chamber 5. Therefore, these particulates are contained in exhaust gas. These particulates contained in the exhaust gas contacts and deposits on a surface of a carrier layer, for example, the surface of the active oxygen releaser 61 as indicated by reference numeral 62 in Fig. 5B, when the exhaust gas is flowing through the exhaust gas inflow passageways 50 of the particulate filter 22 or when the exhaust gas moves from the exhaust gas inflow passageway 50 to the exhaust gas outflow passageway 51.

[0065] When the particulate 62 deposits on the surface of the active oxygen releaser 61 in this way, an oxygen concentration falls on a contact surface between the particulate 62 and the active oxygen releaser 61. When the oxygen concentration thus falls, a concentration difference occurs between the contact surface and a high oxygen concentration in the active oxygen releaser 61, whereby oxygen in the active oxygen releaser 61 tends to move to the contact surface between the particulate 62 and the active oxygen releaser 61. As a result, potassium nitrate (KNO3) formed in the active oxygen releaser 61 is decomposed into potassium (K) and oxygen (O). The oxygen (O) moves to the contact surface between the particulate 62 and the active oxygen releaser 61, and the nitrogen monoxide (NO) is released to the outside from the active oxygen releaser 61. The nitrogen monoxide (NO) released to the outside is oxidized on platinum (Pt) on its downstream side and absorbed in the active oxygen releaser 61 again.

[0066] In addition, it is appeared that active oxygen is also generated in a reaction process with oxygen and oxidize the particulate 62, when oxygen and NOx in exhaust gas are occluded in an oxygen-excessive state. Although a detailed mechanism for this phenomenon is unclear, it is generally assumed as follows.

[0067] As described above, NO in exhaust gas reacts with O_2 - or O^2 - on the surface of platinum Pt to become NO_2 (2NO+ $O_2 \rightarrow 2NO_2$). Subsequently, a part of the generated (NO₂) turns into (NO₃) and is absorbed in the active oxygen releaser 61 while being oxidized on platinum (Pt).

[0068] A part of the NO₂ is decomposed by a catalyst and release active oxygen. That is, the NO₂ repeats oxidation and decomposition in such as follows to release active oxygen;

$$2\mathsf{NO}_2{\rightarrow}\mathsf{NO+O^*}{\rightarrow}\mathsf{NO+O}_2{\rightarrow}\mathsf{NO+O^*}{\rightarrow}.$$

[0069] On the other hand, at this point, potassium sulfate (K_2SO_4) formed in the active oxygen releaser 61 is also decomposed into potassium K, oxygen (O) and (SO_2) . The oxygen (O) moves to the contact surface between the particulate 62 and the active oxygen releaser 61 and the SO_2 is released to the outside from the active oxygen releaser 61. The (SO_2) released to the outside is oxidized on platinum (Pt) on its downstream side and absorbed in the active oxygen releaser 61 again. However, since potassium sulfate (K_2SO_4) is stable, it is hard to release active oxygen compared with potassium nitrate (KNO_3) .

[0070] The Oxygen (O) moving to the contact surface between the particulate 62 and the active oxygen releaser 61 is oxygen decomposed from compounds such as potassium nitrate (KNO₃) or potassium sulfate (K₂SO₄). The oxygen (O) decomposed from a compound has high energy and has extremely high activity. Therefore, the oxygen moving to the contact surface between the particulate 62 and the active oxygen releaser 61 has turned into active oxygen (O). When such active oxygen (O) contacts the particulate 62, the particulate 62 is oxidized in a short time (within a few minutes to several tens of minutes) without emitting luminous flames and completely disappears. Therefore, the particulate 62 never deposits on the particulate filter 22.

[0071] When particulates that deposit on the particulate filter 22 in a laminated shape is burned in the conventional art, the particulate filter 22 glows and burns accompanied with flames. Such burning accompanied with flames does not continue unless it is under a high temperature. Therefore, temperature of the particulate filter 22 must be maintained high in order to cause the burning accompanied with flames to continue.

[0072] To the contrary, in the present invention, the particulate 62 is oxidized without emitting luminous flames as described above, when the surface of the par-

ticulate filter 22 does not glow. That is, in other words, in the present invention, the particulate 62 is oxidized and removed at a considerably low temperature compared with the conventional art. Therefore, a particulate removing action by oxidation of the particulate 62 without emission of luminous flames according to the present invention is completely different from a particulate removing action by burning of the conventional art that is accompanied with flames.

[0073] In addition, the particulate removing action by oxidation of particulates is performed at a considerably low temperature. Therefore, the temperature of the particulate filter 22 does not rise so high, whereby there is almost no risk of the particulate filter 22 deteriorating.

[0074] Moreover, since particulates hardly deposit on the particulate filter 22, a risk of that concentration of ash which is cinder of particulates is lower. Therefore, a risk of clogging the particulate filter 22 being becomes lower.

[0075] Incidentally, the clogging is caused mainly by calcium sulfate (CaSO₄). That is, fuel and lubricating oil contain calcium (Ca) and, therefore, calcium (Ca) is contained in exhaust gas. If SO3 exists, the calcium (Ca) generates calcium sulfate (CaSO₄). Calcium sulfate (CaSO₄) is solid and is not thermally decomposed even if it is heated. Therefore, when calcium sulfate (CaSO₄) is generated and the pores of the particulate filter 22 are blocked by the calcium sulfate (CaSO₄), the clogging is caused.

[0076] However, in this case, if an alkali metal or an alkali-earth metal having ionization tendency higher than that of calcium (Ca), for example, potassium (K) is used as the active oxygen releaser 61, SO_3 dispersed in the active oxygen releaser 61 combines with potassium (K) to form potassium sulfate (K_2SO_4). Calcium (Ca) flows out into the exhaust gas outflow passageways 51 through the partitions 54 of the particulate filter 22 without combining with SO_3 . As a result, the pores of the particulate filter 22 are not clogged any more. Therefore, it is preferable to use an alkali metal or an alkali-earth metal having ionization tendency higher than that of calcium (Ca), that is, potassium (K), lithium (Li), cesium (Cs) or barium (Ba) as the active oxygen releaser 61 as described above.

[0077] Moreover, since potassium sulfate (K_2SO_4) formed on the particulate filter 22 instead of ash has a low concentration compared with calcium sulfate $(CaSO_4)$, it can be easily decomposed and removed by raising an atmospheric temperature of the particulate filter 22 or by placing the particulate filter 22 under a reducing atmosphere.

[0078] Incidentally, in practice, it is almost impossible to reduce an amount of discharged particulates M to be less than an amount of particulates that can be oxidized and removed G in all operation states. For example, a temperature of the particulate filter 22 is usually low at the start of an engine. Therefore, the amount of discharged particulates M is usually greater than the

amount of particulates that can be oxidized and removed G in this case. When the amount of discharged particulates M becomes greater than the amount of particulates that can be oxidized and removed G as immediately after the start of an engine, particulates that were not oxidized starts to remain on the particulate filter 22. **[0079]** In this way, the amount of discharged particulates M is increased to be greater than the amount of particulates that can be oxidized and removed G, and particulates may deposit on the particulate filter 22 in a laminated shape in some cases.

[0080] In order to oxidize and remove the particulates that deposit on the particulate filter 22, the switching valve 71 disposed in the exhaust pipe 70 is switched. When the switching valve 71 is switched, the exhaust upstream side and the exhaust downstream side of the particulate filter 22 are reversed. In a part that was the exhaust downstream side of the particulate filter 22 before switching the switching valve 71, particulates deposit on the surface of the active oxygen releaser 61 and active oxygen (O) is released, whereby the particulates are oxidized and removed. A part of the released active oxygen O moves to the exhaust downstream side of the particulate filter 22 together with exhaust gas and oxidize and remove particulates that deposit there. Here, as described above, the particulates are disturbed in the forward flow direction and the back flow direction on both the side of the particulate filter 22 and move around on both the sides of the particulate filter 22 or inside the base material to meet activated points all over the film base material to be oxidized.

[0081] In this way, when particulate that was not oxidized start to deposit on the particulate filter 22, particulates can be completely oxidized and removed from the particulate filter 22 by reversing the exhaust upstream side and the exhaust downstream side of the particulate filter 22.

[0082] In addition, if particulates deposit on the particulate filter 22, the particulates is oxidized without emitting luminous flames by causing an air-fuel ratio of a part of or entire exhaust gas to be rich temporarily. When the air-fuel ratio of the exhaust gas is made rich, that is, when an oxygen concentration in the exhaust gas is decreased, active oxygen (O) is released to the outside from the active oxygen releaser 61 without interruption. The particulates that deposit on the particulate filter 22 is burnt and removed in a short time (within a few minutes to several tens of minutes) without emitting luminous flames.

(Other embodiments)

[0083] Although a collecting material is described as a material capable of purifying NOx and oxidizing particulates in the above-mentioned embodiment, it is not limited to the above-mentioned one and any material can be adopted as long as it is a filter for collecting particulate matters such as soot and unburnt fuel compo-

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nents in exhaust gas.

[0084] In addition, a dummy converter or the like may be further provided upstream of an exhaust system, thereby trapping phosphorous utilizing a characteristic that phosphorous tends to be absorbed in a place where a flow of exhaust gas is disturbed or in a first member. [0085] Further, although a diesel engine is described in this embodiment as an example of an internal combustion engine to which the exhaust gas purifier in accordance with the present invention is applied, it is needless to mention that the exhaust gas purifier may be applied to a gasoline engine.

[0086] In the case of a gasoline engine, since a sulfur (S) component contained in fuel is less but a phosphorous (P) component is contained in a greater amount compared with those in the case of a diesel engine, calcium (Ca) and the phosphorous (P) component tend to combine with each other to generate calcium phosphate $(Ca_3(PO_4)_2)$ on a particulate filter.

[0087] According to the present invention, as described above, a metal having an electronegativity equal to or lower than that of calcium (Ca) and strong ionization tendency (e.g., potassium (K)) is loaded on an ash trap provided upstream of the particulate filter, whereby combining of potassium (K) or the like with the phosphorous (P) component is given preference over the combining of calcium (Ca) with the phosphorous (P) component and thus generation of $(Ca_3(PO_4)_2)$ is inhibited. Therefore, the exhaust gas purifier in accordance with the present invention is extremely effective for used in a gasoline engine.

[0088] In the exhaust gas purifier for an internal combustion engine in accordance with the present invention is provided with an ash trap loaded with a basic metal upstream of a collecting material, a component to be combined that forms ash when it combines with a predetermined component is given preference in combining with the metal compared with the predetermined component. Thus, formation of ash is inhibited.

[0089] Therefore, according to the present invention, in the exhaust gas purifier provided with the collecting material for collecting particulate matters in exhaust gas, it becomes possible to inhibit formation of ash, so that clogging of the collecting material by ash is prevented and a function of the collecting material can be prevented from being damaged.

[0090] Thus, it is seen that an exhaust gas purifier for an internal combustion engine is provided. One skilled in the art will appreciate that the present invention can be practiced by other than the preferred embodiments which are presented for the purposes of illustration and not of limitation, and the present invention is limited only by the claims which follow.

Claims

1. An exhaust gas purifier for an internal combustion

engine, comprising

a collecting material for collecting particulate matters contained in exhaust gas discharged from the internal combustion engine and

an ash trap for absorbing phosphorous (P) in exhaust gas being provided upstream of said collecting material.

2. An exhaust gas purifier for an internal combustion engine according to claim 1,

wherein said ash trap is loaded with basic metal.

3. An exhaust gas purifier for an internal combustion engine according to claim 1 or 2,

wherein said ash trap is provided with an oxidation performance.

4. An exhaust gas purifier for an internal combustion engine according to any one of claims 1 to 3,

wherein said collecting material is loaded with metal which have an electronegativity equal to or lower than that of a predetermined component contained in fuel or lubricating oil of the internal combustion engine.

5. An exhaust gas purifier for an internal combustion engine according to claim 4,

wherein said metal is selected such that compound of said metal and said predetermined component are discomposed or removed under the same conditions as purification conditions of said particulate matters.

6. An exhaust gas purifier for an internal combustion engine according to claim 1, further comprising

a first exhaust passage way connected to one side of said collecting material.

a second exhaust passage way connected to the other side of said collecting material and

an exhaust switching means for flowing exhaust gas to said first exhaust passage way or second exhaust passage way selectively,

wherein said ash trap is provided in said first exhaust passage way and second exhaust passage way.

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Fig. 1

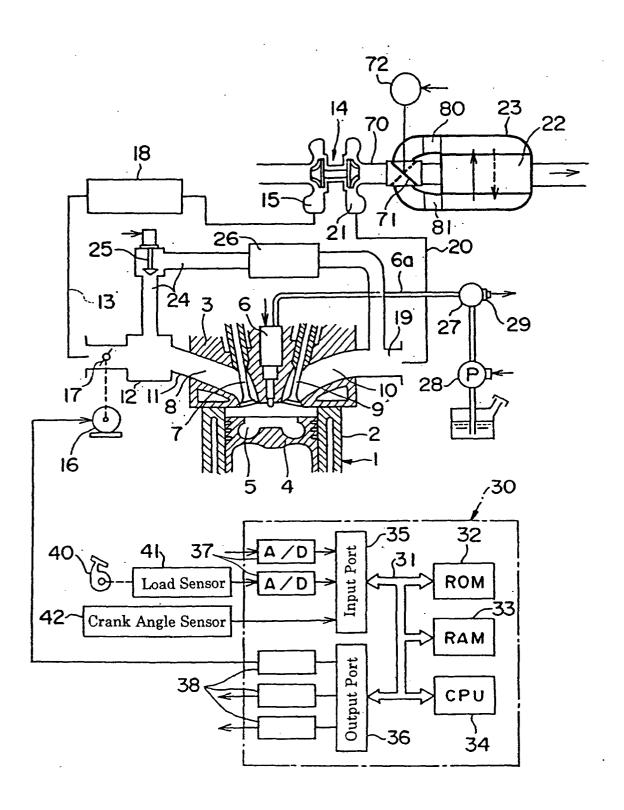


Fig. 2

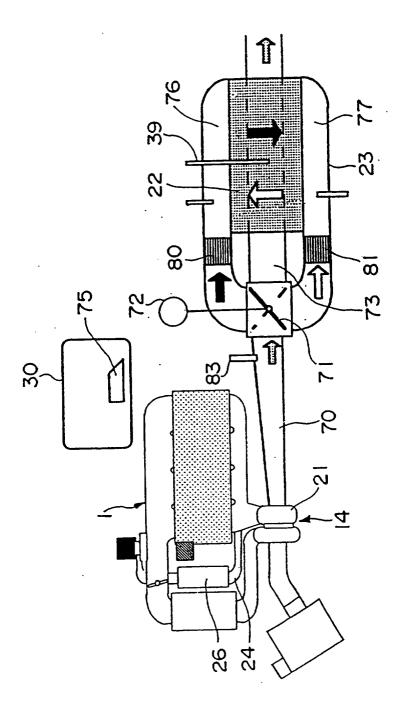
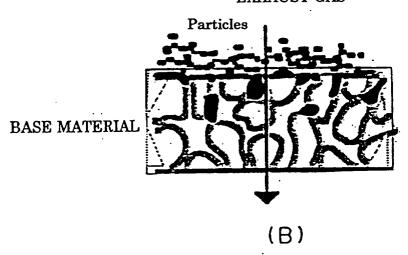


Fig. 3

(A)

EXHAUST GAS



BASE MATERIAL

Particles

Particles

EXHAUST GAS

Fig. 4

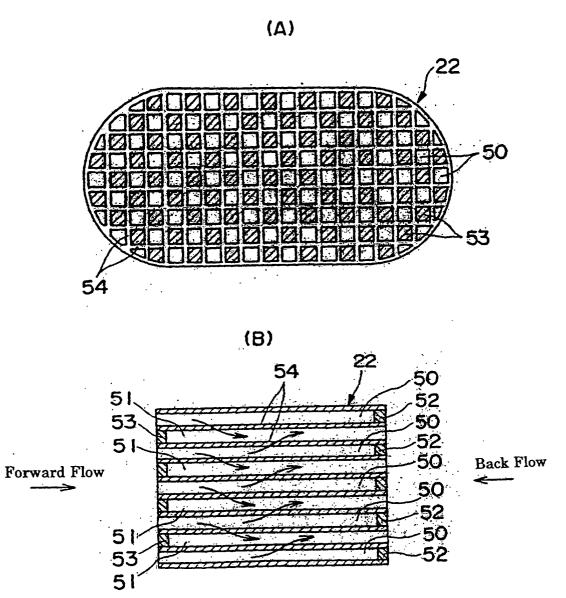
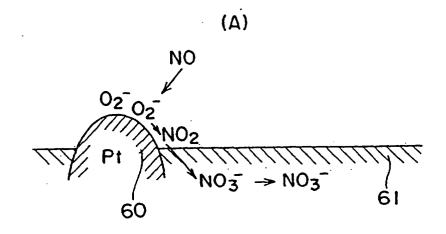
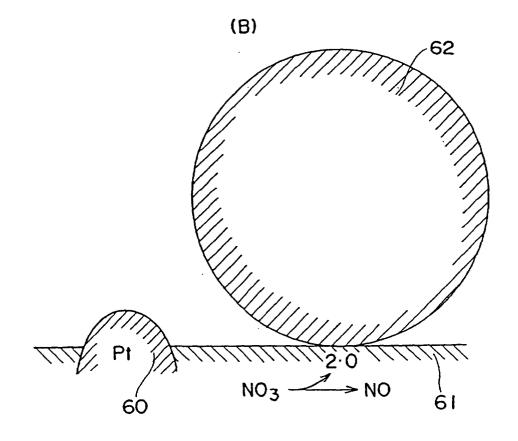


Fig. 5







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