(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 849 853 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
31.10.2007 Bulletin 2007/44

(51) Int Cl.:
C10M 159/18 *(2006.01)*

(21) Application number: **06114706.2**

(22) Date of filing: **30.05.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **27.04.2006 JP 2006308901**

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Remarks:
Amended claims 1-14 in accordance with Rule 86 (2) EPC.

(54) **Additive for engine oil, engine oil, and exhaust gas purifying method**

(57) It is an object of the present invention to provide an additive for engine oil which exists as an exhaust gas purifying catalyst in an exhaust gas purifying filter when provided in a combustion chamber of an internal combustion engine and introduced into the exhaust gas purifying filter together with exhaust gases, after burning of the fuel, and can promote burning of PM, using the catalytic action of the exhaust gas purifying catalyst. The additive for engine oil of the present invention comprises: a compound containing a metallic element, wherein a metal oxide obtained by oxidizing the metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine.

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Description

TECHNICAL FIELD

[0001] The present invention relates to: an additive for engine oil to be added to engine oil as a catalyst component used for assisting combustion of, in particular, particulate matter (hereinafter, referred to also as PM) so as to purify exhaust gases discharged from an internal combustion engine such as a diesel engine; the engine oil to which the additive has been added; and an exhaust gas purifying method that is conducted so as to purify (convert) toxic components in the exhaust gases.

BACKGROUND ART

[0002] Recently, PM, such as soot, contained in exhaust gases that are discharged from internal combustion engines, such as diesel engines, have raised serious problems as influences harmful to the environment and the human body. For this reason, various applications in which honeycomb structured bodies, which are made from porous ceramics using silicon carbide, cordierite or the like as materials, are used as filters for capturing PM in exhaust gases to purify the exhaust gases have been proposed.

[0003] Among exhaust gas purifying filters, those in which an exhaust gas purifying catalyst, such as an oxide catalyst and a noble metal catalyst, is supported have been proposed. In the filter having such an exhaust gas purifying catalyst supported thereon, toxic gas components such as CO, NO and HC in the exhaust gases can be converted (oxidized) by the action of such a catalyst, and the burning temperature of the PM is lowered so that the PM can be burned more efficiently.

[0004] Figs. 6 (a) to (d) are schematic diagrams that schematically show various states which occur at a partition wall portion of a honeycomb structuredbodywhen the exhaust gas purifying filter made of the honeycomb structured body is arranged in a pipe connected to the engine in the prior art structure.

Fig. 6 (a) is a schematic diagram that shows a state in which an exhaust gas purifying catalyst is supported on an exhaust gas purifying filter made of a honeycomb structured body, and Fig. 6(b) is a schematic diagram that shows a state in which the filter is covered with PM and the like.

[0005] In the exhaust gas purifying filter of the above-mentioned type, an exhaust gas purifying catalyst 61 is supported on each of the partition wall portion 60 of the exhaust gas purifying filter made of an unused honeycomb structured body so as to contribute to purification (conversion) of the exhaust gases (see Fig. 6(a)). Here, the exhaust gas purifying catalyst 61 is also supported on the inside of each wall; however, in this figure, the catalyst inside the wall is omitted.

When exhaust gases are introduced into the honeycomb structured body, the PM in the exhaust gases is captured, and accumulated on the surface and the like of the exhaust gas purifying filter (see Fig. 6(b)).

[0006] It is necessary for the collected PM 62 to be regularly burned and eliminated (the filter to be regenerated), and for such a process, for example, a post injection system is mainly used.

At this time, the catalyst supported as described above is made in contact with the PM so that the burning temperature of the PM is lowered and the PM is efficiently burned.

[0007]

Patent Document 1: JP-A 2002-303121
Patent Document 2: JP-A 2000-319679

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] Here, in the engine, engine oil is used for the purposes such as protecting, cooling and sealing sliding portions, and the engine oil contains a large amount of additives such as calcium salt serving as a cleaning agent. A portion of the additive is introduced into the combustion chamber through the piston side wall of the engine, and after having been burned, is captured by the exhaust gas purifying filter together with PM in the exhaust gases.

[0009] When the PM is burned and eliminated, with the above-mentioned additive being captured onto each of the partition wall portion 60 of the exhaust gas purifying filter, one portion of the additive components, made from calcium or the like, remains on the partition wall portion 60 of the exhaust gas purifying filter as ashes 63 without beingburned. Moreover, after the regenerating processes have been repeatedly conducted on the partition wall portion 60 of the exhaust gas purifying filter, the ashes 63 are gradually accumulated to eventually cover the entire exhaust gas purifying catalyst 61 supported on the partition wall portion 60 of the exhaust gas purifying filter (see Fig. 6(c)).

[0010] Here, in addition to those derived from the additive as described above, ashes include, for example, those

caused by abrasion of the sliding portions of the engine and those derived from sulfates and the like generated during the burning process.

[0011] In the case where the engine is further driven in this state to cause a fixed amount of PM 62 accumulated on the ashes 63 as shown in Fig. 6(d), although a regenerating process that burns the PM 62 needs to be carried out, the PM 62 is not allowed to contact to the exhaust gas purifying catalyst 61, with the result that the PM 62 is burned insufficiently.

[0012] When the entire exhaust gas purifying catalyst 61 is thus covered with the ashes 63, the exhaust gas purifying catalyst 61 is not made in contact with the PM accumulated on the filter to cause the problem that its effects as the PM burning catalyst are lowered.

[0013] In order to solve this problem, the invention disclosed in Patent Document 1 has proposed a method in which the flow-in and flow-out directions of the exhaust gases to and from the exhaust gas purifying filter are switched so that the accumulated ashes can be discharged from the filter together with exhaust gases.

[0014] In the above-mentioned invention, however, the structure of pipes used for introducing exhaust gases into the exhaust gas purifying filter becomes complicated to cause the capacity of a casing in which the filter is installed to become larger; therefore, when the limited installation space in which the casing has to be placed is taken into consideration, this structure is not suitable. Moreover, a controlling mechanism used for switching directions is further required to cause a problem of high costs. Furthermore, the ashes accumulated on the walls are highly viscous, and are hardly discharged by a pressure derived from the exhaust gases.

[0015] Moreover, in Patent Document 2, disclosed is an invention proposing use of an engine oil with a powder of cerium oxide added thereto so that cerium oxide is used as an exhaust gas purifying catalyst in a combustion chamber of an engine.

[0016] However, when the engine oil with cerium oxide particles added thereto is used, there was a problem that sufficient catalytic action was not exerted after being accumulated on the filter.

It can be considered that this is because the specific surface area of the cerium oxide particle has become small by sintering and the like, and the lattice defect of oxygen has decreased.

MEANS FOR SOLVING THE PROBLEMS

[0017] As a result of earnest study in view of the above-mentioned problems, the inventors of the present invention found out that, when an engine oil with an additive for engine oil added thereto is used, the additive for engine oil comprising a compound containing a metallic element, wherein a metal oxide obtained by oxidizing the metallic element is a compound having a catalytic action which promotes burning of PM contained in exhaust gases discharged from an internal combustion engine, the metal oxide is introduced into an exhaust gas purifying filter with the exhaust gases after the fuel is burned, so that it exists as a catalyst which promotes burning of PM particularly on the filter to promote burning of PM using the catalytic act ion of the existing metal oxide, and completed an additive for engine oil of the present invention. In addition, the present inventors completed an invention concerning an engine oil which contains the above-mentioned additive, and an invention concerning an exhaust gas purifying method in which exhaust gases are purified even after ashes have been accumulated, by making the metallic oxide exist in and/or on the ashes accumulated on the exhaust gas purifying filter so that the metal oxide comes into contact with the PM.

[0018] Namely, an additive for engine oil of the first aspect of the present invention comprises: a compound containing a metallic element, wherein a metal oxide obtained by oxidizing the metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine.

[0019] Further, the additive for engine oil of the present invention is desirably used for providing the metal oxide in a filter of an exhaust gas purifying device connected to a combustion chamber of the internal combustion engine.

[0020] An additive for engine oil of the second aspect of the present invention comprises: a compound containing a metallic element, wherein the compound containing a metallic element comprises a metal complex including at least one kind of metallic element selected from the group consisting of 4th period elements, lanthanoids, and 4th group elements in the periodic table.

[0021] Further, the additive for engine oil of the first or second aspect of the present invention is desirably a metal complex represented by a general formula (1) :

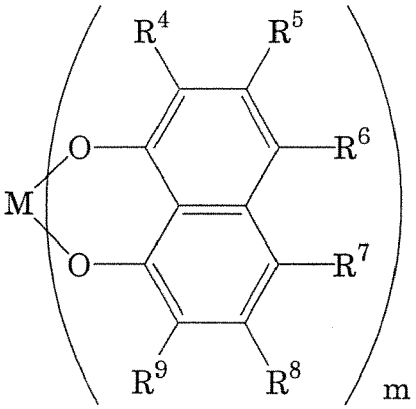
$$M(OR^1)_p(R^2COCHCOR^3)_q \qquad (1)$$

(wherein M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn;
each of p and q represents a whole number determined such that the metal complex has a coordination number of 2 to 8, or p or q may be 0;
each of R^1, each of R^2, or each of R^3 may be the same, or may differ when the number of R^1, R^2, or R^3 is 2 or more; and R^1 and R^2 independently represent an alkyl group with a carbon number of 1 to 6, and R^3 represents an alkyl group with

a carbon number of 1 to 6 and/or an alkoxy group with a carbon number of 1 to 16).

[0022] In the additive for engine oil of the first or second aspect of the present invention, desirably, R^1 and R^2 in the general formula (1) independently represent: at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group, and R^3 represents: at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group; and/or at least one kind selected from the group consisting of a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, a tert-butoxy group, a 2-ethylhexyloxy group, and a lauryloxy group.

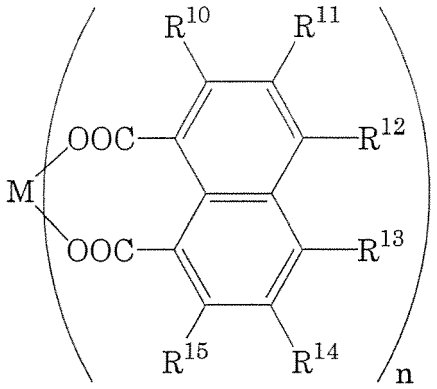
[0023] The additive for engine oil of the first or second aspect of the present invention is desirably a metal complex represented by the following formula (2) :



...(2)

(wherein R^4 to R^9 independently represent a hydrogen or the alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and m is 1 or 2)

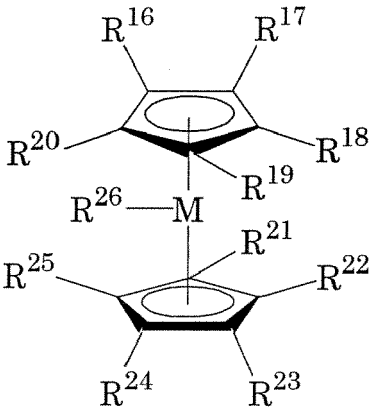
[0024] The additive for engine oil of the first or second aspect of the present invention is desirably a metal complex represented by the following formula (3):



...(3)

(wherein R^{10} to R^{15} independently represent hydrogen or the alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and n is 1 or 2)

[0025] The additive for engine oil of the first or second aspect of the present invention is desirably a metal complex represented by the following formula (4):



. . . (4)

(wherein R^{16} to R^{25} independently represent a hydrogen or the alkyl group, wherein R^{26} is a hydrogen or does not exist, and M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn)

[0026] In the additive for engine oil of the first or second aspect of the present invention, desirably, the metallic element is cerium.

[0027] In the additive for engine oil of the first or second aspect of the present invention, desirably, the compound containing a metallic element is a metal complex which has a trivalent or tetravalent cerium ion as a central metal.

[0028] An engine oil of the third aspect of the present invention comprises the additive for engine oil composed of any of the above-mentioned compounds containing a metallic element.

[0029] In the engine oil of the present invention, desirably, the added amount of the additive for engine oil is 1 to 10% by weight.

[0030] An exhaust gas purifying method of the fourth aspect of the present invention comprises: an exhaust gas purifying method using an additive for engine oil comprising a compound containing a metallic element, wherein an engine oil including the additive for engine oil is used, a metal oxide obtained by oxidizing the metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine, and the metal oxide is provided in the filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine by introducing the compound containing a metallic element into the combustion chamber of the internal combustion engine to purify exhaust gases using the catalytic action of the metal oxide provided in the filter of the exhaust gas purifying device.

[0031] In the exhaust gas purifying method, desirably, the filter of the exhaust gas purifying device is a honeycomb structured body comprising: a plurality of cells in the longitudinal direction with a cell wall therebetween; and a plug that seals either one of the ends of the cell so that exhaust gases flow through the cell wall.

EFFECTS OF THE INVENTION

[0032] The additive for engine oil of the first aspect of the present invention comprising a compound containing a metallic element can be dissolved in engine oil, thereby, after being introduced into a combustion chamber of the engine, and when an ash is accumulated on the exhaust gas purifying filter, exists as a metal oxide in the ash and/or on the ash, so that it can function as a catalyst for promoting burning of PM.

Even after the engine is driven for a long period of time and PM is accumulated, a catalyst deriving from the engine oil can come into contact with the PM to assist burning of PM (regeneration of the filter) . As a result, regenerating rate of the filter can be improved.

[0033] The regeneration rate of the exhaust gas purifying filter refers to how close the weight of the exhaust gas purifying filter which increased from accumulated PM becomes by regenerating process to the weight immediately after the last regeneration, and the more the weight of the exhaust gas purifying filter subjected to the regenerating process is close to the weight of the exhaust gas purifying filter immediately after the last regeneration, the higher the regeneration rate is.

[0034] The additive for engine oil of the second aspect of the present invention comprising a compound containing a metallic element can be dissolved in engine oil, since it serves as a metal complex, thereby, after being introduced into a combustion chamber of the engine, and when an ash is accumulated on the exhaust gas purifying filter, exists as a metal oxide in the ash and/or on the ash, so that it can function as a catalyst for promoting burning of PM.

Even after the engine is driven for a long period of time and PM is accumulated, a catalyst deriving from the engine oil can come into contact with the PM to assist burning of PM (regeneration of the filter). As a result, regenerating rate of the filter can be improved.

[0035] The engine oil of the third aspect of the present invention includes the additive for engine oil of the first or second aspect of the present invention comprising a compound containing a metallic element; therefore, when this engine oil is used, after the engine oil is introduced into a combustion chamber of the engine, and when an ash is accumulated on the exhaust gas purifying filter, a metal oxide can exist in the ash and/or on the ash, so that it can function as a catalyst for promoting burning of PM.
Even after the engine is driven for a long period of time and PM is accumulated, a catalyst deriving from the engine oil can come into contact with the PM to assist burning of PM (regeneration of the filter). As a result, regenerating rate of the filter can be improved.

[0036] In the exhaust gas purifying method of the fourth aspect of the present invention, a compound containing a metallic element is added to an engine oil; therefore, after the engine oil is introduced into a combustion chamber of the engine, and when an ash is accumulated on the exhaust gas purifying filter, a metal oxide can exist in the ash and/or on the ash, so that it can function as a catalyst for promoting burning of PM.
Even after the engine is driven for a long period of time and PM is accumulated, a catalyst deriving from the engine oil can come into contact with the PM to assist burning of PM (regeneration of the filter) . As a result, regenerating rate of the filter can be improved.
According to this method, without installing a special exhaust gas purifying device or using a special operating method, purification of exhaust gases can be carried out efficiently over a long period of time with the same exhaust gas purifying filter.

BEST MODE FOR CARRYING OUT THE INVENTION

[0037] First, an additive for engine oil of the first aspect and the second aspect of the present invention, as well as an engine oil of the third aspect of present invention, to which the above-mentioned additive for engine oil is added, will be described.
Hereinafter, in the present specification, as long as there is no particular notice, the first aspect of the present invention and the second aspect of the present invention are described without distinction.

[0038] The additive for engine oil of the first aspect of the present invention comprises: a compound containing a metallic element, wherein a metal oxide obtained by oxidizing the metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine.

[0039] The additive for engine oil of the second aspect of the present invention comprises: a compound containing a metallic element, wherein the compound containing a metallic element comprises a metal complex including at least one kind of metallic element selected from the group consisting of 4th period elements, lanthanoids, and 4th group elements in the periodic table.

[0040] The additive for engine oil of the present invention is used by being added to an engine oil; the engine oil is that in which an additive such as a cleaning agent, a abrasion-proof agent, a dispersing agent, a viscosity index improving agent, a pour point depressant (superplasticizer), and an antioxidant is added to a mineral oil, a chemical synthetic oil, or a partial synthetic oil serving as a base oil at the rate of 15 to 30% by weight in total of the whole mixture, and those having various combinations are commercially available.

[0041] Among the additives, as a cleaning agent, a metallic cleaning agent is mostly used, examples thereof including: neutral salt which is an alkaline earth metal salt of organic acids, such as fatty acids having carbon numbers of 8 to 22, or an overbased compound containing a carbonate of alkaline earth metal salt (particularly calcium salt, magnesium salt), and normally about 0.5 to 10% by weight thereof is added to the engine oil.
Metallic components such as the above-mentioned calcium and magnesium turn into a component of the ash which is accumulated on the exhaust gas purifying filter.

[0042] Although the additive for engine oil is an additive used as one kind of additive added to the engine oil, as of the above-mentioned additives, in order to use the additive as an additive for engine oil, the additive is desirably capable of dissolving in the base oil, or dispersing in the base oil in a colloid-like form.
In a case where the additive for engine oil cannot be dissolved or dispersed in the base oil, the additive component precipitates at the bottom of a container which stores the engine oil, thereby it becomes difficult to inject the additive component into the engine. Even if injection is possible, the flowability of the engine oil is obstructed within the engine, resulting in the worst case that destruction of the engine may occur.

[0043] As the additive for engine oil, desirably, a compound containing a metallic element whose oxide functions as a catalyst which promotes burning of PM is used.
Moreover, the additive for engine oil is desirably capable of being used for providing the metal oxide in the filter of the exhaust gas purifying device connected to the combustion chamber of the internal combustion engine.

[0044] Although the type of the metallic element is not particularly limited, a metallic element selected from the group consisting of 4th period elements, lanthanoids, and 4th group elements in the periodic table is desirably used, and particularly, one kind of metallic element selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and

Sn is desirably used as the metallic element.

The additive for engine oil may contain in the compound two or more kinds of different metallic elements among the above-mentioned metallic elements. It may also be an additive which is a mixture of two or more kinds of compounds, each of which contain different metallic elements among the above-mentioned metallic elements.

Moreover, when two or more kinds of different metallic elements are contained in the additive for engine oil, the two or more kinds of different metallic elements may be two or more kinds of metallic elements whose multiple oxide functions as a catalyst which promotes burning of PM.

[0045] Although the type of the compound containing a metallic element is not particularly limited, from the viewpoint of availability and stability, a complex having an alcohol represented by R^1OH (wherein R^1 represents an alkyl group having a carbon number of 1 to 6) and a diketone represented by $R^2COCH_2COR^3$ (wherein R^2 represents an alkyl group having a carbon number of 1 to 6, and R^3 represents an alkyl group having a carbon number of 1 to 6, or an alkoxy group having a carbon number of 1 to 16) as ligands is suitably used. A more desirable complex is a metal complex having a diketone as a ligand. With the complex having diketones as ligands, ametal complex soluble to the engine oil can be prepared.

[0046] In the present invention, an organometallic complex, a complex compound containing a metallic element, a coordination compound containing a metallic element, a metallic complex salt (salt containing a metallic element and a complex ion), a metal cluster, a cluster complex, a metal cluster complex, and a compound containing any of these complexes, are generically referred to as a metal complex.

[0047] Further, the additive for engine oil is desirably a metal complex represented by a general formula (1):

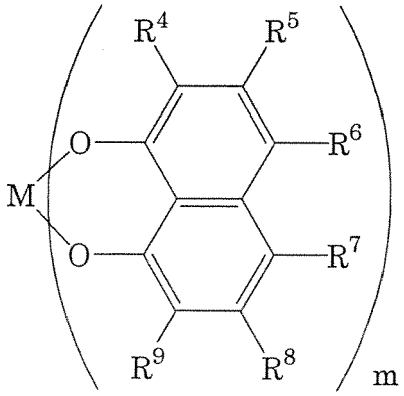
$$M(OR^1)_p(R^2COCHCOR^3)_q \qquad (1)$$

(wherein M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn;
each of p and q represents a whole number determined such that the metal complex has a coordination number of 2 to 8 or p or q may be 0;
each of R^1, each of R^2, or each of R^3 may be the same, or may differ when the number of R^1, R^2, or R^3 is 2 or more; and R^1 and R^2 independently represent an alkyl group with a carbon number of 1 to 6, and R^3 represents an alkyl group with a carbon number of 1 to 6 and/or an alkoxy group with a carbon number of 1 to 16) .

[0048] In the additive for engine oil, desirably, R^1 and R^2 in the general formula (1) independently represent: at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group, and R^3 represents: at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group; and/or at least one kind selected from the group consisting of a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, a tert-butoxy group, a 2-ethylhexyloxy group, and a lauryloxy group.
For example, when the general formula represents $Ce(OR^1)_3(R^2COCHCOR^3)_1$, the three ($OR^1$) may differ from each other, such as (OCH_3) (OC_2H_5) (O-iso-C_3H_7).

[0049] Although a specific example of these metal complexes is not what is limited to below, examples thereof include: $Ce(O\text{-iso-}C_3H_7)_3$, $Ce(O\text{-iso-}C_3H_7)_4$, $Ce(O\text{-tert-}C_4H_9)_4$, $Ce(OCH_2CH_2OCH_3)_4$, $Ce(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, $Ce(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_4$, $Ce(O\text{-iso-}C_3H_7)_2(CH_3\text{-}CO\text{-}CH{=}COCH_3)_2$, $Ce(O\text{-iso-}C_3H_7)_2(C_2H_5OCO\text{-}CH{=}COCH_3)_2$, $Ce(CH_3OCO\text{-}CH{=}COCH_3)_4$, $Ce(tert\text{-}C_4H_9\text{-}CO\text{-}CH{=}CO\text{-}tert\text{-}C_4H_9)_4$, $Cu(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$, $Pb(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$, $Ni(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$, $V(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, $Cr(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, $Mn(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, $Fe(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, $CO(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$, and $Sn(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$.

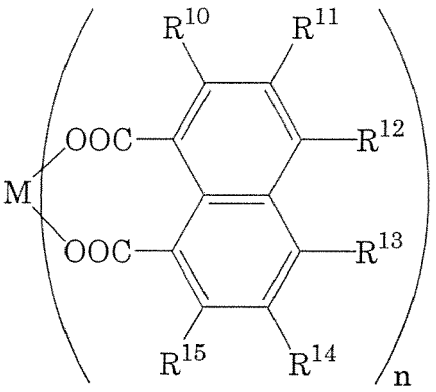
[0050] As a compound containing a metallic element, 1, 8-naphthalenediolates represented by the following formula (2) :



...(2)

(wherein R^4 to R^9 independently represent a hydrogen or an alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and m is 1 or 2) is also suitably used.
By using such complex salt with a ligand having a naphthalene nucleus, a metal complex soluble to the engine oil can be obtained.

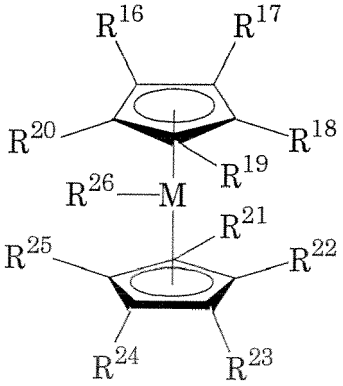
[0051] As a compound containing a metallic element, 1, 8-naphthalene-dicarboxylic-acid salts represented by the following formula (3):



...(3)

(wherein R^{10} to R^{15} independently represent a hydrogen or an alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and n is 1 or 2) is also suitably used.
By using such complex salt with a ligand having a naphthalene nucleus, a metal complex soluble to the engine oil can be obtained.

[0052] As a compound containing a metallic element, a bis-cyclopentadienyl complex salt represented by the following formula (4):



. . . (4)

(wherein R^{16} to R^{25} independently represent a hydrogen or an alkyl group, R^{26} is a hydrogen or does not exist, and M is selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn) is also suitably used.
By using such complex salts, the metal complex can serve as a compound containing a metallic element which is soluble to the engine oil.

[0053] Among the above-mentioned metallic elements, particularly, a compound containing cerium is desirably used as the additive for engine oil of the present invention. The reason is because the compound containing cerium is widely used as a catalyst which promotes burning of PM, and functions as a catalyst which promotes burning of PM when accumulated and existing on the exhaust gas purifying filter.

[0054] Here, the exhaust gas purifying function of the cerium compound will be described.
It is known that the cerium compound functions as an exhaust gas purifying catalyst particularly because of its oxygen storage ability. Specifically, the cerium compound has a function to release oxygen by the reaction of $2CeO_2 \rightarrow Ce_2O_3+1/2O_2$, and a function to occlude the oxygen by a reverse reaction thereof.
At the time of burning the PM, oxygen required for the burning is provided so that burning of the PM is promoted; thus the burning temperature of PM can be lowered, leading to decrease in energy required for filter regeneration.

[0055] Therefore, the cerium compound is desirably composed as an additive having a form which can be dissolved or dispersed in the base oil.
In particular, a metal complex having a trivalent or tetravalent cerium ion as the central metal is desirably added thereto, and as the metal complex having the trivalent cerium ion, the metal complexes represented by the general formula (1) or 4 are proposed. As the metal complex having the tetravalent cerium ion, the metal complexes represented by the general formula (1), (2) or (3) are proposed.

[0056] In the present invention, these compounds containing a metallic element may be used by one kind, or may be used in a desired combination of two or more kinds. Moreover, a partial hydrolysate of these compounds can also be used.

[0057] The additive for engine oil of the first and second aspect of the present invention comprising a compound containing a metallic element can be dissolved in the engine oil since the complex salt soluble to the organic solvent having a hydrophobic ligand is used. Thus, when the engine oil of the third aspect of present invention with the same additive added thereto is used, the additive component can be easily introduced into the inner part of the engine.

[0058] The added amount of the additive for engine oil to the engine oil is desirably 1 to 10% by weight. With the added amount of less than 1%, the amount at which the additive as a catalyst comes into contact with the PM becomes small, which tends to decrease the effect which promotes burning of PM, and when the added amount is more than 10%, the flowability of oil tends to become poor.

[0059] The metallic element contained in the additive in the engine oil enters the combustion chamber of an engine, and together with burning of a fuel, is oxidized thereafter to become a metal oxide so that it is introduced into the exhaust gas purifying filter with the PM in exhaust gases. Note that the exhaust gas purifying method using the additive for engine oil will be described later in detail.

[0060] On the basis of the above-mentioned description, it can be said that the metal oxide functions as a catalyst for promoting burning of the PM. Through the filter regenerating process, if the metal oxide exists on a filter as an ash, the metal oxide functions as an exhaust gas purifying catalyst on the filter and as a catalyst for promoting burning of PM.
Even after the engine is driven for a long period of time and PM is accumulated, the catalyst deriving from the engine oil can come into contact with the PM to assist the burning of PM (regeneration of the filter) . As a result, the regeneration rate of the filter can be improved.

[0061] Next, the exhaust gas purifying method of the fourth aspect of the present invention will be described.
The exhaust gas purifying method of the fourth aspect of the present invention comprises: an exhaust gas purifying method using an additive for engine oil comprising a compound containing a metallic element, wherein an engine oil

including the additive for engine oil is used, a metal oxide obtained by oxidizing the metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine, and the metal oxide is provided in the filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine by introducing the compound containing a metallic element into the combustion chamber of the internal combustion engine to purify exhaust gases using the catalytic action of the metal oxide provided in the filter of the exhaust gas purifying device.

[0062] That is, in the fourth aspect of the present invention, first, using the engine oil with the compound containing a metallic element added thereto, the compound containing a metallic element is introduced into the combustion chamber of the internal combustion engine so that, together with the PM generated by burning the fuel, the metal oxide is accumulated on the inside of the filter of the exhaust gas purifying device connected to the combustion chamber of the internal combustion engine.

Hereinafter, description will be given of a case using a diesel engine as the internal combustion engine, and an engine oil added thereto a cerium compound as the compound containing a metallic element.

[0063]

Fig. 1 is a view that schematically shows one part of a diesel engine, and an exhaust gas purifying device connected to the diesel engine.

Figs. 2(a) to (d) are schematic diagrams that schematically show various states which occur at a partition wall portion of a honeycomb structured body when the exhaust gas purifying filter comprising the honeycomb structured body is arranged in a pipe connected with the engine in the fourth aspect of the present invention.

Although in the fourth aspect of the present invention the filter of the exhaust gas purifying device is not particularly limited, in Fig. 1, an aggregated honeycomb structured body 40 is provided as a filter.

Description of the aggregated honeycomb structured body will be given later in detail.

[0064] When a diesel engine 81 is driven, first an intake valve 82 opens, and while piston 89 descends from an upper dead point, an intake port 83 draws air into a combustion chamber 93.

Then, intake valve 82 closes, and while piston 89 ascends from a bottom dead point, the air drawn into the combustion chamber 93 is compressed so that it becomes high temperature.

[0065] To the air which was compressed in this way and became a high temperature of 600°C or more, a fuel whose pressure is enhanced to 100 atm or more is injected from a fuel injection pump 86, to make the fuel burn by self-ignition so that the piston 89 descends.

When the piston 89 falls to the bottom dead point through burning, an exhaust valve 84 opens, and while the piston 89 ascends from the bottom dead point, exhaust gas (combustion gas) is discharged from an exhaust port 85.

Considering the above-mentioned process as one cycle, a crank shaft 91 rotates two times in one cycle, and thereby, force is obtained.

[0066] Here, an engine oil 92 has a roll to prevent wearing out and overheating of the piston 89 and an outer wall portion 87 of the engine, both of which are made of metal, due to the piston 89 and the outer wall portion 87 made into contact with one another, together with a roll to prevent leakage of compressed gas and explosion gas by filling the gap between the piston 89 and the outer wall portion 87. However, some of the engine oil 92 leak out into the combustion chamber 93 from the gap between the piston 89 and the outer wall portion 87, and is burned with the fuel.

During this process, the additives added in the engine oil 92 are also applied to burning and an inflammable additive is burned off; however, a non flammable additive such as a metallic cleaning agent is discharged from the exhaust port 85 without being burned.

[0067] With respect to the cerium compound added to the engine oil 92, while the chemical structure thereof changes with burning, as a cerium metal it is not burned off, but is discharged from the exhaust port 85 with the exhaust gas, mainly in the form of a cerium oxide.

[0068] The exhaust port 85 and the like of the diesel engine 81 is connected to an introducing pipe 24 of an exhaust gas purifying device 200, the aggregated honeycomb structured body 40 is placed in a metal casing 23 of the exhaust gas purifying device 200, so that it serves as a flowpath of the exhaust gas, and an exhaust pipe 25 is connected to the outside of the other end of the exhaust purifying device 200. In Fig. 1, the arrows show the flow of the exhaust gas.

[0069] Therefore, the exhaust gas generated in the diesel engine 81 is introduced into the inner part of the filter (the aggregated honeycomb structured body 40) through the exhaust port 85 and the introducing pipe 24, so that the PM in the exhaust gas is captured by the aggregated honeycomb structured body 40.

Here, the cerium oxide and the noncombustible additive such as the metallic cleaning agent which have been discharged with the exhaust gas from the exhaust port 85, are also captured by the aggregated honeycomb structured body 40, together with the PM.

[0070] If a predetermined amount of PM is accumulated thereafter, the pressure loss will become large to affect the engine; thus, a regenerating process of the filter accompanied by burning of the PM, is carried out. Even after this

regenerating process, the cerium oxide remains in the ash inside the aggregated honeycomb structured body 40 to thereafter be made in contact with the accumulated PM, thereby functioning as a catalyst for promoting burning of the PM. The catalytic action of the accumulated cerium oxide can thus promote burning of the PM.

[0071] Normally, an exhaust gas purifying catalyst is previously supported on the aggregated honeycomb structured body 40. Such case will be described using Fig. 2.

First, on a partition wall portion 60 of the honeycomb structured body with an exhaust gas purifying catalyst 61 supported thereon as shown in Fig. 2(a), when exhaust gases pass, PM in the exhaust gases is captured and accumulate on the surface of the filter, as shown in Fig. 2(b). Here, since the supported catalyst and the PM are made into contact, PM is readily burned according to the effect of the catalyst.

[0072] The captured PM 72 needs to be burned and removed (the filter needs to be subjected to the regenerating process) periodically, and a post-injection system is mainly used for such processing.

[0073] When the regenerating process for burning and removing the PM 72 is carried out, cerium oxides 73 remain with ashes 63, as shown in Fig. 2(c).

When the regenerating process of the filter is repeatedly carried out, the PM 72 and the cerium oxides 73 are accumulated on the ashes 63, as shown in Fig. 2(d), and the surface of the exhaust gas purifying catalyst 61 supported on the filter will be covered with the ashes 63; thus the exhaust gas purifying catalyst 61 supported on the filter can not be made into contact with the PM 72. Even in such a case, there exists a portion in which the cerium oxide 73 is exposed in the uppermost surface of the ashes. Since this cerium oxide 73 can contact with the PM 72, it can function as a catalyst for promoting burning of the PM. As a result, the burning temperature of the PM can be lowered and the regeneration rate of the filter improves.

[0074] In the fourth aspect of the present invention, the type of filter for the exhaust gas purifying device is not particularly limited, and for example, a honeycomb structured body comprising a plurality of cells formed in the longitudinal direction with a cell wall therebetween, and a plug for sealing either one of the ends of the cells so that exhaust gases pass through the cell wall, may be used.

[0075] The above-mentioned honeycomb structured body can be divided generally into types as follows: a honeycomb structured body in which a plurality of honeycomb fired bodies having plural cells formed in the longitudinal direction with a cell wall therebetween, either one of the ends of the cell being sealed with a plug, are bound together through a sealing material layer (adhesive layer) to form a ceramic block with a sealing material layer (coat layer) formed on the periphery thereof (herein after, this type is also referred to as an aggregated honeycomb structured body); and a honeycomb structured body comprising a single honeycomb fired body in which plural cells are longitudinally formed with a cell wall therebetween, and with either one of the ends of the cell being sealed with a plug (hereinafter, this type is also referred to as an integral honeycomb structured body).

[0076] Fig. 3 is a perspective view that schematically shows one example of the aggregated honeycomb structured body, Fig. 4(a) is a perspective view showing a honeycomb fired body that constitutes the honeycomb structured body shown in Fig. 3, and Fig. 3(b) is a cross-sectional view taken along line B-B of the honeycomb fired body shown in Fig. 3(a).

[0077] As shown in Fig. 3, in the aggregated honeycomb structured body 40, a plurality of honeycomb fired bodies 50 made from silicon carbide-based ceramic or the like are combined with each other through a sealing material layer (adhesive layer) 41 to form a cylindrical ceramic block 43, and a sealing material layer (coat layer) 42 is formed on the periphery of this ceramic block 43.

[0078] In the aggregated honeycomb structured body 40 shown in Fig. 3, the shape of the ceramic block is cylindrical; however, in the honeycomb structured body, the shape of the ceramic block is not limited to a cylindrical shape as long as it is pillar-shaped and, for example, it may be a cylindroid shape, a rectangular pillar-shape, or any other desired shape.

[0079] As shown in Figs. 4(a) and 4(b), the honeycomb fired body 50 has a structure in which a plurality of cells 51 are placed in parallel with one another in the longitudinal direction with a cell wall 53 therebetween, with either one of the end portions of the cell 51 being sealed with a plug 52 and, the cell wall 53 that separates the cells 51 are allowed to function as filters. In other words, each of the cells 51 formed in the honeycomb fired body 50 has either one of the end portions on the inlet side or the outlet side of exhaust gases sealed with the plug 52 as shown in Fig. 4(b) so that exhaust gases that have flowed into one of the cells 51 are always allowed to flow out of another cell 51 after having passed through the cell wall 53 that separates the cells 51.

[0080] The aggregated honeycomb structured body 40 is mainly made of porous ceramics, and with respect to the material, examples thereof include: nitride ceramics such as aluminum nitride, silicon nitride, boron nitride and titanium-nitrideand the like; carbide ceramics such as silicon carbide zirconium carbide, titanium carbide, tantalum carbide, tungsten carbide and the like; and oxide ceramics such as alumina, zirconia, cordierite, mullite, silica, aluminum titanate and the like. Further, the honeycomb fired body may be formed by a composite body between silicon and silicon carbide. In the case where the composite body between silicon and silicon carbide is used, silicon is desirably added thereto so as to be set to 0 to 45% by weight in the entire body.

In particular, when the aggregated honeycomb structured body is used as a filter, a silicon carbide-based ceramic material which is superior inheat resistance, mechanical characteristics and has a high thermal conductivity, is desirably

used as the material of the honeycomb fired body. Here, the silicon carbide-based ceramic refers to a material having a silicon carbide content of 60% by weight or more.

[0081] With respect to the thickness of the cell wall 53, the lower limit value is desirably set to 0.1 mm and the upper limit value is desirably set to 0.4 mm.

The thickness of the cell wall 53 being less than 0.1 mm tends to cause a reduction in strength of the cell wall 53, thereby causing damages such as cracks and the like, and on the other hand, with the thickness of the cell wall 53 exceeding 0.4 mm, a high aperture ratio can not be maintained, which tends to cause an increase in the pressure loss as a result.

[0082] The porosity of the aggregated honeycomb structured body 40 is desirably in the range of 40 to 60%.

The porosity of less than 40% tends to cause increase in the pressure loss, while the porosity exceeding 60% tends to cause reduction in strength.

Here, the above-mentioned porosity can be measured through known methods such as a mercury injection method using a mercury porosimeter, Archimedes method, a measuring method using a scanning electronic microscope (SEM) and other methods.

[0083] The average pore diameter of the aggregated honeycomb structured body 40 is not particularly limited, and the lower limit value is desirably set to 1 μm, and the upper limit value is desirably set to 50 μm. It is more desirable that the lower limit value is set to 5 μm, and the upper limit value is set to 30 μm. The average pore diameter of less than 1 μm tends to cause an increase in pressure loss, and on the other hand, with the average pore diameter exceeding 50 μm, PM readily passes through the pores leading to insufficient capturing of the PM, which tends to cause a reduction in capturing efficiency of PM.

[0084] The plug 52 and the cell wall 53 that seal the aggregated honeycomb structured bodies 40 are desirably made from the same porous ceramic material. With this arrangement, the contact strength between the two members is increased, and by adjusting the porosity of the plug 52 in the same manner as the cell walls 53, the coefficient of thermal expansion of the cell walls 53 and the coefficient of thermal expansion of the plug 52 are properly adjusted so that it becomes possible to prevent a gap from being generated between the plug 52 and the cell walls 53 due to a thermal stress upon production and in use and also to prevent cracks from occurring in the plug 52 and at portions of the cell walls 53 that are made in contact with the plug 52.

[0085] With respect to the length of the plug 52, although not particularly limited, in the case where the plug 52 is made from porous silicon carbide, the lower limit value is desirably set to 1 mm, and the upper limit value is desirably set to 20 mm.

The length of the plug of less than 1 mm results in cases that the end portion of the cell can not be sealed surely, while the length exceeding 20 mm tends to reduce the effective filtration area in the honeycomb structured body.

[0086] In the aggregated honeycomb structured body 40, the sealing material layer (adhesive layer) 41, which is formed between the honeycomb fired bodies 50, has a function of preventing exhaust gases from leaking, and further functions as a bonding material used for binding a plurality of the honeycomb fired bodies 50 to one another. In contrast, the sealing material layer (coat layer) 42, which is formed on the peripheral face of the ceramic block 43, is also allowed to function as a sealing material used for preventing exhaust gases passing through the cells from leaking from the peripheral face of the ceramic block 43 when the aggregated honeycomb structured body 40 is placed in an exhaust passage of an engine, and as an reinforcing member for adjusting the shape of the ceramic block 43 as well as reinforcing the outer periphery thereof.

[0087] Here, in the aggregated honeycomb structured body 40, the adhesive layer 41 and the coat layer 42 may be formed by using the same material, or may be formed by using different materials. In the case where the adhesive layer 41 and the coat layer 42 are made from the same material, the compounding ratio of materials thereof may be the same or different. Moreover, the material may have either a dense structure or a porous structure.

[0088] With respect to the material used for forming the adhesive layer 41 and the coat layer 42, not particularly limited, for example, a material, made from an inorganic binder and an organic binder as well as inorganic fibers and/or inorganic particles, may be used.

[0089] With respect to the above-mentioned inorganic binder, for example, silica sol and alumina sol may be used. Each of these materials may be used alone, or two or more kinds of these may be used in combination. Of the above-mentioned inorganic binders, silica sol is more desirably used.

[0090] With respect to the organic binder, examples thereof include: polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose and the like. Each of these may be used alone or two or more kinds of these may be used in combination. Among the organic binders, carboxy methyl cellulose is more desirably used.

[0091] With respect to the inorganic fibers, examples thereof include: ceramic fibers such as alumina, silica, silica-alumina, glass, potassium titanate, aluminum borate and the like, and whiskers such as alumina, silica, zirconia, titania, ceria, mullite, silicon carbide and the like. Each of these may be used alone, or two or more kinds of these maybe used in combination. Among the inorganic fibers, alumina fibers are more desirably used.

[0092] With respect to the inorganic particles, for example, carbides, nitrides and the like may be used, and more specifically, inorganic fine powder, made from silicon carbide, siliconnitride, boron nitride or the like, may be used. Each

of these may be used alone, or two or more kinds of these may be used in combination. Among the above-mentioned inorganic particles, silicon carbide, which is superior in thermal conductivity, is more desirably used.

[0093] Moreover, a pore-forming agent, such as balloons that are fine hollow spheres composed of oxide-based ceramics, spherical acrylic particles and graphite, may be added to the above-mentioned paste used for forming the sealing material layer, if necessary.

With respect to the above-mentioned balloons, not particularly limited, for example, alumina balloons, glass micro-balloons, shirasuballoons, flyashballoons (FAballoons), mullite balloons and the like may be used. Among these, alumina balloons are more desirably used.

[0094] Further, a catalyst is supported on the aggregated honeycomb structured body. As the catalyst, for example, a noble metal such as platinum, palladium, rhodium and the like may be used as a noble metal catalyst, and also an alkali metal, an alkali earth metal and an oxide may be used. These may also be used in combination.

Moreover, as an oxide catalyst, a metal oxide such as CeO_2 ZrO_2, FeO_2, Fe_2O_3, CuO, CuO_2, Mn_2O_3, MnO and the like, as well as a composite oxide represented by a composition formula $A_nB_{1-n}CO_3$ (wherein A is La, Nd, Sm, Eu, Gd or Y; B is alkali metal or alkali earth metal; and C is Mn, Co, Fe or Ni) and the like may be used. When the oxide catalyst is supported on the honeycomb structured body, the catalyst comes into contact with the PM, thereby reducing the burning temperature of the PM.

[0095] Moreover, when the above-mentioned catalyst is adhered to the aggregated honeycomb structured body, the catalyst may be adhered thereto after the surface has been preliminarily coated with a catalyst supporting layer made of alumina or the like. Thus, the specific surface area of the honeycomb structured body can be enlarged and the dispersivity of the catalyst can be enhanced, to increase the reaction site of the catalyst. Further, the catalyst supporting layer can prevent the catalytic metal from sintering.

[0096] Examples of the material for the catalyst supporting layer include oxide ceramics, such as alumina, titania, zirconia, silica and the like.

[0097] While the present invention can be applied to a honeycomb structured body in which the catalyst is not previously supported thereon, more desirably the catalyst is to be supported on the honeycomb structured body. With the catalyst not being previously supported, the catalytic amount will be insufficient when burning the PM before a certain amount of catalyst deriving from the engine oil is piled up, and the burning temperature is thereby increased, causing poor burning efficiency.

[0098] Next, the following description will discuss a manufacturing method of the aggregated honeycomb structured body.

First, an extrusion-molding process is carried out by using material paste mainly composed of the above-mentioned ceramic material so that a square-pillar shaped ceramic molded body is manufactured.

[0099] Although the material paste is not particularly limited, a material paste in which the porosity of the manufactured honeycomb fired body is set in the range of 40 to 60% is desirably used. For example, a material paste in which a binder, a dispersant solution and the like is added to powder composed of the ceramics mentioned above may be used.

[0100] With respect to the particle size of ceramic powder, although not particularly limited, those which are less susceptible to shrinkage in the succeeding firing process are desirably used, and for example, those powders, prepared by combining 100 parts by weight of powders having an average particle diameter about 3 to 70 μm with 5 to 65 parts by weight of powders having an average particle diameter about 0.1 to 1.0 μm, are preferably used.

Here, the ceramic powder may be subjected to an oxidizing process.

[0101] With respect to the above-mentioned binder, not particularly limited, examples thereof include: methylcellulose, carboxy methylcellulose, hydroxy ethylcellulose, polyethylene glycol, phenolic resin, epoxy resin and the like.

In general, the compounding amount of the above-mentioned binder is desirably set to about 1 to 15 parts by weight with respect to 100 parts by weight of the ceramic powder.

[0102] With respect to the dispersant solution, not particularly limited, examples thereof include: an organic solvent such as benzene and the like; alcohol such as methanol and the like; water, and the like.

An appropriate amount of the above-mentioned dispersant solution is mixed therein so that the viscosity of the material paste is set within a fixed range.

[0103] These ceramic powder, binder and dispersant solution are mixed by an attritor or the like, and sufficiently kneaded by a kneader or the like, and then extrusion-molded.

[0104] Moreover, a molding auxiliary may be added to the material paste, if necessary.

With respect to the molding auxiliary, not particularly limited, examples thereof include ethylene glycol, dextrin, fatty acid, fatty acid soap, polyvinyl alcohol and the like.

[0105] Moreover, a pore-forming agent, such as balloons that are fine hollow spheres composed of oxide-based ceramics, spherical acrylic particles and graphite, may be added to the above-mentioned material paste, if necessary.

With respect to the above-mentioned balloons, not particularly limited, for example, alumina balloons, glass micro-balloons, shirasuballoons, flyashballoons (FAballoons), mullite balloons and the like may be used. Among these, alumina balloons are more desirably used.

[0106] Next, the above-mentioned ceramic molded body is dried by using a drier such as a microwave drier, a hot-air drier, a dielectric drier, a reduced-pressure drier, a vacuum drier and a frozen drier so that a ceramic dried body is formed. Thereafter, a predetermined amount of plug paste, which forms plugs, is injected into the end portion on the outlet side of the inlet-side group of cells and the end portion on the inlet side of the outlet-side group of cells so that the cells are sealed.

[0107] With respect to the plug paste, although not particularly limited, such paste as to set the porosity of a plug produced through the succeeding processes to 30 to 75% is desirably used, and for example, the same paste as the material paste may be used.

Moreover, in this process, the length of the plug formed through the subsequent processes can be adjusted by adjusting the amount of the paste to be inserted.

[0108] Next, the ceramic dried body filled with the plug paste is subjected to degreasing (for example, 200 to 500°C) and firing processes (for example, 1400 to 2300°C) under predetermined conditions so that a honeycomb fired body 50 constituted by a single sintered body as a whole, and having a plurality of cells placed in parallel along the longitudinal direction with a cell wall therebetween, either one of the end portion of the cell being sealed, can be manufactured.

With respect to the degreasing and firing conditions of the ceramic dried body, it is possible to apply conditions that have been conventionally used for manufacturing a filter made from porous ceramics.

[0109] Next, an adhesive paste to form the adhesive layer 41 is applied to each of the side faces of the honeycomb fired body 50 with an even thickness to form an adhesive paste layer, and by repeating a process for successively laminating another honeycomb fired body 50 on this adhesive paste layer, a honeycomb fired body aggregated body having a predetermined size is manufactured.

In order to obtain space between the honeycomb fired bodies 50, a method in which a space holding material is attached onto the honeycomb fired body 50 so that plural honeycomb fired bodies 50 are put together through space holding materials to produce an aggregated body and thereafter the adhesive paste is injected into the space between the honeycomb fired bodies 50, may also be applied.

With respect to the material for forming the adhesive paste, since it has already been explained, explanation thereof is omitted here.

[0110] Next, the aggregated body of the honeycomb fired bodies is heated so that the adhesive paste layer is dried and solidified to form the adhesive layer 41.

Then, the aggregated body of the honeycomb fired bodies in which a plurality of the honeycomb fired bodies 50 are bonded to one another through the adhesive layers 41 is subjected to a cutting process by using a diamond cutter and other tools so that a ceramic block 43 having a cylindrical shape is manufactured.

[0111] By forming a sealing material layer 42 on the periphery of the ceramic block 43 by using the sealing material paste, an aggregated honeycomb structured body 40 in which the sealing material layer 42 is formed on the outer peripheral portion of the cylindrical ceramic block 43 having a plurality of the honeycomb fired bodies 50 bonded to one another through the adhesive layers 41.

[0112] Thereafter, according to need, a catalyst is supported on the honeycomb structured body. The supporting process of the catalyst may be carried out on the honeycomb fired body prior to the formation of the aggregated body. When supporting the catalyst, desirably, an alumina film having a high specific surface area is formed on the surface of the honeycomb structured body, and a catalyst such as a co-catalyst, platinum and the like is adhered to this alumina film.

[0113] With respect to the method for forming the alumina film on the aggregated honeycomb structured body, for example, a method in which the honeycomb structured body is impregnated with a solution of a metal compound containing aluminum such as $Al(NO_3)_3$ and the like and then heated, and a method in which the honeycomb structured body is impregnated with a solution containing alumina powder and then heated, and other methods are proposed.

With respect to the method for adhering the co-catalyst, for example, a method in which the honeycomb structured body is impregnated with, for example, a solution of metal compound containing a rare earth element and the like such as Ce $(NO_3)_3$ and the like and then heated, and other methods are proposed.

With respect to the method for adhering the catalyst, for example, a method in which the honeycomb structured body is impregnated with, for example, a solution of diammine dinitro platinum nitric acid ($[Pt(NH_3)_2(NO_2)_2]HNO_3$, platinum concentration: 4.53% by weight) and the like and then heated is proposed.

Moreover, the catalyst may be adhered by using a method in which the honeycomb structured body is impregnated with a compound containing alumina powder with a catalyst previously adhered to the alumina particles, and then heated.

[0114] Further, instead of forming the alumina film, oxides may be supported. As the above-mentioned oxide, examples thereof include a metal oxide such as CeO_2, ZrO_2, FeO_2, Fe_2O_3, CuO, CuO_2, Mn_2O_3, MnO and the like, and a composite oxide represented by a composition formula $A_nB_{1-n}CO_3$ (wherein A is La, Nd, Sm, Eu, Gd or Y; B is alkali metal or alkali earth metal; and C is Mn, Co, Fe or Ni) . Each of these may be used alone, or two or more kinds of these may be used in combination.

[0115] Next, the integral honeycomb structured body will be described.

The integral honeycomb structured body consists of a honeycomb structured body manufactured in an integrated form,

wherein the whole honeycomb structured body is not bound through adhesives and the like. Therefore, the integral honeycomb structured body can be considered as a honeycomb structured body constituted by one of the honeycomb fired bodies which comprises the aggregated honeycomb structured body. However, its size is the same as that of the aggregated honeycomb structured body, and its shape is a required shape as a honeycomb structured body, namely shapes such as a cylindrical shape, cylindroid shape and the like.

[0116] Consequently, the structure, the required characteristics and the like of the integral honeycomb structured body is almost the same as that of the aggregated honeycomb structured body described above, and the manufacturing method thereof is almost the same as the method for manufacturing the honeycomb fired body. However, a sealing material layer may also be provided afterwards on the periphery of such a sintered body.

Moreover, the material used for the ceramic preferably is low in coefficient of expansion, and has difficulty forming cracks and the like and, for example, cordierite, aluminum titanate and the like is preferably used.

[0117] The aggregated honeycomb structured body and the integral honeycomb structured body are normally set into a cylindrical metal casing. The material for the metal casing, for example, may be metals such as stainless steel, iron and the like. The shape of the metal casing may be a single-type tubiform, or a separable tubiform (for example, a clamshell-type metal casing and the like) which can be separated into two or more parts.

EXAMPLES

[0118] The following description will discuss the present invention in detail by means of examples; however, the present invention is not intended to be limited by these examples.

(Example 1)

(Preparation of engine oil with compound containing metallic element added thereto)

[0119] To 100 parts by weight of commercial engine oil (base oil, commercial mineral oil (paraffin-based mineral oil), viscosity: 120 mm^2/s•40°C) was added 1 part by weight of cerium (IV) 1,8-naphthalene-dicarboxylate (hereinafter, referred to also as 1,8-NDCA) (hereinafter, referred to as additive 1) to prepare a mixed material.

(Production of aggregated honeycomb structured body)

[0120] Coarse powder of α-type silicon carbide having an average particle diameter of 22 μm (7000 parts by weight) and fine powder of α-type silicon carbide having an average particle diameter of 0.5 μm. (3000 parts by weight) were wet-mixed, and to 10000 parts by weight of the resulting mixture were added and kneaded 550 parts by weight of an organic binder (methyl cellulose), 330 parts by weight of a plasticizer (UNILUB, made by NOF Corp.), 150 parts by weight of glycerin serving as a lubricant and 2000 parts by weight of water to obtain a mixed composition, and this was then extrusion-molded to manufacture a raw molded body having a rectangular pillar shape as shown in Fig. 4.

[0121] Next, after the above-mentioned raw molded body had been dried by using a microwave drier or the like to prepare a ceramic dried body, predetermined cells were filled with a plug material paste having the same composition as the raw molded body.

After this had been again dried by using a drier, the resulting product was degreased at 400°C, and fired at 2200°C in a normal-pressure argon atmosphere for 3 hours to manufacture a honeycomb fired body 50, which was a silicon carbide sintered body with a porosity of 42% and an average pore diameter of 11 μm, having a size of 34.3 mm $\times$ 34.3 mm $\times$ 150 mm, the number of cells 51 (cell density) of 31 pcs/cm^2 (200 pcs/in^2) and a thickness of the cell walls 53 of 0.40 mm.

[0122] By using a heat resistant adhesive paste containing 30% by weight of alumina fibers having an average fiber length of 20μm, 21% by weight of silicon carbide particles having an average particle diameter of 0.6 μm, 15% by weight of silica sol, 5.6% by weight of carboxy methyl cellulose and 28.4% by weight of water, a number of the honeycomb fired bodies 50 were bonded to one another, and this was dried at 120°C and then cut by using a diamond cutter so that a cylindrical ceramic block 43 having a thickness of the adhesive layer of 1 mm was manufactured.

[0123] Next, silica-alumina fibers (average fiber length: 100 μm, average fiber diameter: 10 μm) (23.3% by weight), which served as inorganic fibers, silicon carbide powder having an average particle diameter of 0.3 μm (30.2% by weight), which served as inorganic particles, silica sol (SiO_2 content in the sol: 30% by weight) (7% by weight), which served as an inorganic binder, carboxymethyl cellulose (0.5% by weight), which served as an organic binder, and water (39% by weight) were mixed and kneaded to prepare a sealing material paste.

[0124] Next, a sealing material paste layer having a thickness of 0.2 mm was formed on the peripheral portion of the ceramic block 43 by using the above-mentioned sealing material paste. Further, this sealing material paste layer was dried at 120°C so that a cylindrical aggregated honeycomb structured body 40 having a size of 143.8 mm in diameter $\times$ 150 mm in length (capacity: 2.44 liters) was manufactured.

[0125] Next, the honeycomb structured body was immersed in a solution containing 10 g of CeO_2, 40 ml of water and an appropriate amount of a pH-adjusting agent for 5 minutes, and this was then subjected to a firing process at 500°C so that CeO_2 serving as an oxide catalyst was supported thereon.
Here, the apparent density of the honeycomb fired bodies 50 forming the aggregated honeycomb structured body 40 was 0.49 g/cm^3.

(Assembly of exhaust gas purifying device)

[0126] Moreover, an exhaust gas purifying device used for measuring the regeneration rate and evaluating the exhaust gas purification performance was assembled by using the following method.
Fig. 5 is an explanatory drawing of the exhaust gas purifying device.
The exhaust gas purifying device 270 was prepared as a scanning mobility particle sizer (SMPS) provided with a common-rail-type diesel engine 276 of 2L, an exhaust gas pipe 277 that allows exhaust gases from the engine 276 to flow therein, a metal casing 271 that is connected to the exhaust gas pipe 277 and houses the honeycomb structured body 40, a sampler 278 that samples exhaust gases prior to the flow through the honeycomb structured body, a sampler 279 that samples exhaust gases after the flow through the honeycomb structured body, a diluter 280 that dilutes the exhaust gases that have been sampled by the samplers 278 and 279 and a PM counter 281 (made by TSI Co., Ltd., aggregated particle counter 3022A-S) that measures the amount of PM contained in the diluted exhaust gases.
Although the honeycomb structured body used here is not particularly limited, Fig. 5 shows a view in which the aggregated honeycomb structured body 40 was set therein.
[0127] In the present examples, when the exhaust gas purifying device was assembled, an aggregated honeycomb structured body was used as the honeycomb structured body, and with a hold-sealing member formed around the outer peripheral portion thereof, set in the metal casing.

(Evaluation on exhaust gas purifying performance)

[0128] The following description will discuss a sequence of measuring process.

(Measurements of regenerating rate)

[0129] First, the weight a_0 of an aggregated honeycomb structured body with no PM accumulated thereon was measured. Next, the engine 276 was driven at the number of revolutions of 3000 min^{-1} with a torque of 50 Nm for 5 hours so that PM was accumulated on the aggregated honeycomb structured body. Here, the honeycomb structured body was once taken out, and the weight b_1 thereof was measured. Thus, the weight x (= b_1 - a_0) of PM accumulated during a driving process at one time was calculated.
Thereafter, the engine was driven under a post-injection system for 7 minutes so that the aggregated honeycomb structured body was subjected to a regenerating process, and the weight a_1 of the aggregated honeycomb structured body after the regenerating process was measured.
By using the following calculation equation, the regenerating rate (%) was calculated.

$$\text{Regenerating rate (\%)} = (1 - (a_1 - a_0)/x) \times 100$$

Here, the regenerating rate, calculated after the regenerating process for the first time, was referred to as the first regenerating rate.
This driving and regenerating process was set as one cycle, and this cycle was repeated 200 times, with engine oil being exchanged for every 5 cycles.
In this case, the weight a_{199} of the aggregated honeycomb structured body immediately after the 199th regenerating process and the weight a_{200} of the aggregated honeycomb structured body immediately after the 200th regenerating process were measured.
Then, in the same manner as the first regenerating rate, by using the following calculation equation, the regenerating rate (%) was calculated.

$$\text{Regenerating rate (\%)} = (1 - (a_{200} - a_{199})/x) \times 100$$

The regenerating rate was set as the 200th regenerating rate.

Here, the repeated operations of 200 cycles correspond to the mileage of 100,000 kilometers.

(Example 2)

[0130] The same processes as those of Example 1 were carried out except that the engine oil was prepared by adding 3% by weight of the additive 1 thereto as the compound containing a metallic element, and evaluations were conducted on the exhaust gas purifying performances.

(Example 3)

[0131] The same processes as those of Example 1 were carried out except that the engine oil was prepared by adding 5% by weight of the additive 1 thereto as the compound containing a metallic element, and evaluations were conducted on the exhaust gas purifying performances.

(Example 4)

[0132] The same processes as those of Example 1 were carried out except that the engine oil was prepared by adding 10% by weight of the additive 1 thereto as the compound containing a metallic element, and evaluations were conducted on the exhaust gas purifying performances.

(Examples 5 to 25)

[0133] The same processes as those of Example 1 were carried out except that each of compounds indicated by chemical formulas shown in Table 1 was used as the compound containing a metallic element and that the engine oil was prepared by adding 5% by weight of each of the additives thereto, and evaluations were conducted on the exhaust gas purifying performances.
Here, in Table 1, $(1,8\text{-}C_{10}H_6O_2)_2Ce$ of Example 8 represents a metal complex (cerium (IV)1,8-naphthalenediolate) composed of two molecules of 1,8-naphthalenediolate and cerium (IV).
Moreover, $(C_5H_5)_2$ in Examples 23 to 25 refers to a (bis) cyclopentadienyl group, and additives used in Examples 23 to 25 represent cyclopentadienyl complexes of cerium (III), iron (II) and cobalt (II), respectively.

(Comparative Example 1)

[0134] The same processes as those of Example 1 except that engine oil to which no additive composed of a compound containing a metallic element was added was used, and evaluations were conducted on the exhaust gas purifying performances.

(Reference Example 1)

[0135] The same processes as those of Example 1 were carried out except that the engine oil was prepared by adding 0.5% by weight of the additive 1 thereto as the compound containing a metallic element, and evaluations were conducted on the exhaust gas purifying performances.
[0136] Table 1 shows the results of these examples and comparative examples.
[0137]

Table 1

	Type of additive containing a metallic element	Amount of additive (% by weight)	First regenerating rate (%)	200th regenerating rate (%)
Example 1	$(1,8\text{-NDCA})_2Ce$	1	94	88
Example 2	$(1,8\text{-NDCA})_2Ce$	3	94	91
Example 3	$(1,8\text{-NDCA})_2Ce$	5	95	93
Example 4	$(1,8\text{-NDCA})_2Ce$	10	95	93
Example 5	(1,8-NDCA)Co	5	92	88

(continued)

	Type of additive containing a metallic element	Amount of additive (% by weight)	First regenerating rate (%)	200th regenerating rate (%)
Example 6	$(1,8\text{-NDCA})_2Mn$	5	91	86
Example 7	(1,8-NDCA) Ni	5	92	87
Example 8	$(1,8\text{-}C_{10}H_6O_2)_2Ce$	5	94	92
Example 9	$Ce(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$	5	93	91
Example 10	$Ce(CH_3\text{-}CO\text{-}CH{=}CO\text{-}OCH_3)_4$	5	92	87
Example 11	$Ce(O\text{-iso-}C_3H_7)_3$	5	92	88
Example 12	$Ce(OCH_3)(OC_2H_5)(O\text{-iso-}C_3H_7)$	5	90	87
Example 13	$Ce(O\text{-iso-}C_3H_7)_2(CH_3\text{-}CO\text{-}CH{=}COCH_3)_2$	5	91	87
Example 14	$Cu(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$	5	90	86
Example 15	$Pb(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$	5	92	87
Example 16	$Ni(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$	5	90	86
Example 17	$V(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$	5	91	87
Example 18	$Cr(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$	5	92	88
Example 19	$Mn(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)$	5	90	86
Example 20	$Fe(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3$	5	92	87
Example 21	$Co(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_3$	5	91	87
Example 22	$Sn(CH_3\text{-}CO\text{-}CH{=}CO\text{-}CH_3)_2$	5	92	88
Example. 23	$(C_5H_5)_2CeH$	5	93	91
Example 24	$(C_5H_5)_2Fe$	5	94	86
Example 25	$(C_5H_5)_2Co$	5	93	88
Comparative Example 1	Not added	None	94	62
Reference Example 1	$(1,8\text{-NDCA})_2Ce$	0.5	95	82

(1,8-NDCA): 1,8-naphthalenedicarboxylate group
$(1,8\text{-}C_{10}H_5O_2)_2Ce_2$: cerium(IV)1,8-naphthalenediolate
$(C_5H_5)_2$: (bis)cyclopentadienyl group

[0138] As clearly indicated by the results shown in Table 1, even after the 200th regenerating process, the honeycomb

structured bodies according to the examples made it possible to maintain a high regenerating rate of 86% or more, which was almost equal to the first regenerating process.

[0139] In contrast, in the honeycomb structured body according to Comparative Example 1 although a high regenerating rate was obtained after the first regenerating process, the regenerating rate after the 200th regenerating process was lowered to a level of 60%, which was inferior to the regenerating rate of Examples 1 to 25.

The reason for this is presumably because, since no catalyst exists in accumulated ashes, it is not possible to promote the burning of PM by using the catalyst to fail to sufficiently remove the PM.

BRIEF DESCRIPTION OF THE DRAWINGS

[0140]

Fig. 1 is a view that schematically shows one part of a diesel engine, and an exhaust gas purifying device connected to the diesel engine.

Figs. 2(a) to (d) are schematic diagrams that schematically show various states which occur at a partition wall portion of a honeycomb structured body when the exhaust gas purifying filter comprising the honeycomb structured body is arranged in a pipe connected to the engine in the fourth aspect of the present invention.

Fig. 3 is a perspective view that schematically shows one example of the aggregated honeycomb structured body.

Fig. 4(a) is a perspective view that schematically shows honeycomb fired bodies that form the honeycomb structured body shown in Fig. 3; and Fig. 4(b) is a cross-sectional view taken along line B-B thereof.

Fig. 5 is an explanatory drawing that shows the exhaust gas purifying device that has been assembled in Examples.

Figs. 6(a) to (d) are schematic diagrams that schematically show various states which occur at a partition wall portion of a honeycomb structured body when the exhaust gas purifying filter comprising the honeycomb structured body is arranged in a pipe connected to the engine in the prior art structure.

EXPLANATION OF SYMBOLS

[0141]

23, 271	Metal casing
24	Introducing pipe
25	Exhaust pipe
40	Aggregated honeycomb structured body
50	Honeycomb fired body
51	Cell
53	Cell wall
60	Partition wall portion
61	Exhaust gas purifying catalyst
62, 72	PM
63	Ash
73	Cerium oxide
81, 276	Diesel engine
92	Engine oil
93	Combustion chamber
200, 270	Exhaust gas purifying device

Claims

1. An additive for engine oil comprising:

a compound containing a metallic element,
wherein
a metal oxide obtained by oxidizing said metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine.

2. The additive for engine oil according to claim 1,
wherein

said additive for engine oil is used for providing said metal oxide in a filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine.

3. An additive for engine oil comprising:

a compound containing a metallic element,
wherein
said compound containing a metallic element comprises a metal complex including at least one kind of metallic element selected from the group consisting of 4th period elements, lanthanoids, and 4th group elements in the periodic table.

4. The additive for engine oil according to any of claims 1 to 3,
wherein
said compound containing a metallic element is a metal complex represented by a general formula (1) :

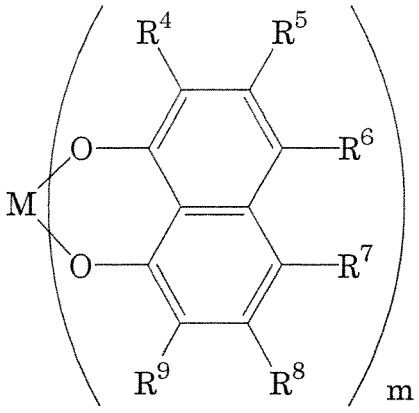
$$M(OR^1)_p(R^2COCHCOR^3)_q \qquad (1)$$

(wherein M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn;
each of p and q represents a whole number determined such that the metal complex has a coordination number of 2 to 8, or p or q may be 0;
each of R^1, each of R^2, or each of R^3 may be the same, or may differ when the number of R^1, R^2, or R^3 is 2 or more; and
R^1 and R^2 independently represent an alkyl group with a carbon number of 1 to 6, and R^3 represents an alkyl group with a carbon number of 1 to 6 and/or an alkoxy group with a carbon number of 1 to 16) .

5. The additive for engine oil according to claim 4,
wherein
R^1 and R^2 in said general formula (1) independently represent:

at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group, and
R^3 represents:
at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group; and/or
at least one kind selected from the group consisting of a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, a tert-butoxy group, a 2-ethylhexyloxy group, and a lauryloxy group.

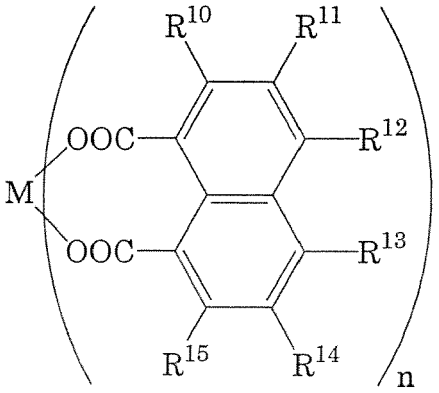
6. The additive for engine oil according to any of claims 1 to 3,
represented by the following formula (2):



...(2)

(wherein R^4 to R^9 independently represent a hydrogen or an alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and m is 1 or 2).

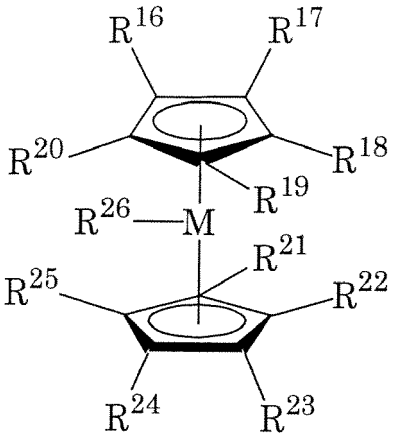
7. The additive for engine oil according to any of claims 1 to 3, represented by the following formula (3):



...(3)

(wherein R^{10} to R^{15} independently represent a hydrogen or an alkyl group, M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn, and n is 1 or 2).

8. The additive for engine oil according to any of claims 1 to 3, represented by the following formula (4) :



...(4)

(wherein R^{16} to R^{25} independently represent a hydrogen or an alkyl group, R^{26} is a hydrogen or does not exist, and M is one kind selected from the group consisting of Ce, V, Cr, Mn, Ni, Co, Cu, Fe, Pb, and Sn).

9. The additive for engine oil according to any of claims 1 to 8, wherein said metallic element is cerium.

10. The additive for engine oil according to claim 1, 2, 3, 4, 5, or 8, wherein said compound containing a metallic element is a metal complex which has a trivalent cerium ion as a central metal.

11. The additive for engine oil according to any of claims 1 to 7, wherein said compound containing a metallic element is a metal complex which has a tetravalent cerium ion as a central metal.

12. An engine oil comprising:

the additive for engine oil according to any of claims 1 to 11.

13. The engine oil according to claim 12,
wherein
the added amount of said additive for engine oil is 1 to 10% by weight.

14. An exhaust gas purifying method using an additive for engine oil comprising a compound containing a metallic element,
wherein
an engine oil including the additive for engine oil is used,
a metal oxide obtained by oxidizing said metallic element has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine, and
said metal oxide is provided in the filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine by introducing said compound containing a metallic element into the combustion chamber of the internal combustion engine
to purify exhaust gases using the catalytic action of said metal oxide provided in the filter of the exhaust gas purifying device.

15. The exhaust gas purifying method according to claim 14,
wherein
said filter of the exhaust gas purifying device is a honeycomb structured body comprising:

a plurality of cells in the longitudinal direction with a cell wall therebetween; and
a plug that seals either one of the ends of said cell so that exhaust gases flow through said cell wall.

Amended claims in accordance with Rule 86(2) EPC.

1. An additive for engine oil

stored in a container in the engine oil and dissolved or dispersed in the engine oil
comprising:

a compound containing cerium,

wherein
a cerium oxide obtained by oxidizing said cerium has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine.

2. The additive for engine oil according to claim 1,
wherein
said additive for engine oil is used for providing said cerium oxide in a filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine.

3. The additive for engine oil according to claim 1 or 2
wherein
said compound containing cerium comprises a metal complex.

4. The additive for engine oil according to any of claims 1 to 3,
wherein
said compound containing cerium is a metal complex represented by a general formula (1):

$$M\ (OR^1)_p(R^2COCHCOR^3)_q \qquad (1)$$

(wherein M is Ce;
each of p and q represents a whole number determined such that the metal complex has a coordination number of

3 to 8, or p or q may be 0;
each of R^1, each of R^2, or each of R^3 may be the same, or may differ when the number of R^1, R^2, or R^3 is 2 or more; and R^1 and R^2 independently represent an alkyl group with a carbon number of 1 to 6, and R^3 represents an alkyl group with a carbon number of 1 to 16).

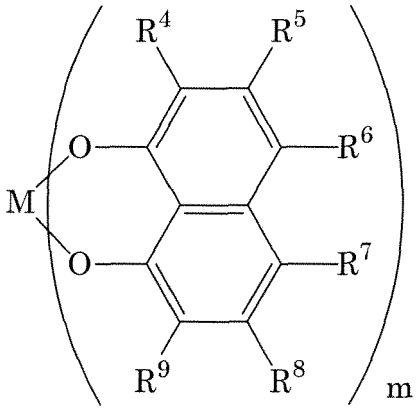
5. The additive for engine oil according to claim 4,
wherein
R^1 and R^2 in said general formula (1) independently represent:

at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group, and

R^3 represents:

at least one kind selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, a tert-butyl group, an n-pentyl group, and a 2-ethoxyethyl group; and/or
at least one kind selected from the group consisting of a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, a tert-butoxy group, a 2-ethylhexyloxy group, and a lauryloxy group.

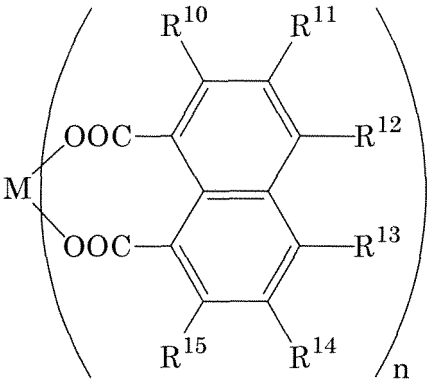
6. The additive for engine oil according to any of claims 1 to 3,
represented by the following formula (2):



...(2)

(wherein R^4 to R^9 independently represent a hydrogen or an alkyl group, M is Ce, and m is 2).

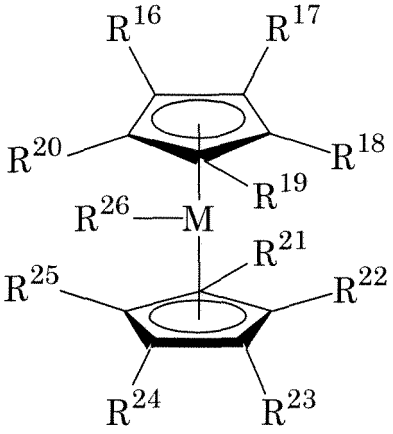
7. The additive for engine oil according to any of claims 1 to 3,
represented by the following formula (3):



...(3)

(wherein R^{10} to R^{15} independently represent a hydrogen or an alkyl group, M is Ce, and n is 2).

8. The additive for engine oil according to any of claims 1 to 3,
represented by the following formula (4):



... (4)

(wherein R^{16} to R^{25} independently represent a hydrogen or an alkyl group, R^{26} is a hydrogen, and M is Ce).

9. The additive for engine oil according to claim 1, 2, 3, 4, 5, or 8,
wherein
said compound containing cerium is a metal complex which has a trivalent cerium ion as a central metal.

10. The additive for engine oil according to any of claims 1 to 7,
wherein
said compound containing cerium is a metal complex which has a tetravalent cerium ion as a central metal.

11. An engine oil comprising:

the additive for engine oil according to any of claims 1 to 10.

12. The engine oil according to claim 11,
wherein
the added amount of said additive for engine oil is 1 to 10% by weight.

13. An exhaust gas purifying method using an additive for engine oil comprising a compound containing cerium,
wherein
an engine oil including the additive for engine oil is used,
a cerium oxide obtained by oxidizing said cerium has a catalytic action which promotes burning of a particulate matter contained in exhaust gases discharged from an internal combustion engine, and
said cerium oxide is provided in the filter of an exhaust gas purifying device connected with a combustion chamber of the internal combustion engine by introducing said compound containing cerium into the combustion chamber of the internal combustion engine
to purify exhaust gases using the catalytic action of said cerium oxide provided in the filter of the exhaust gas purifying device.

14. The exhaust gas purifying method according to claim 13,
wherein
said filter of the exhaust gas purifying device is a honeycomb structured body comprising:

a plurality of cells in the longitudinal direction with a cell wall therebetween; and
a plug that seals either one of the ends of said cell so that exhaust gases flow through said cell wall.

Fig. 1

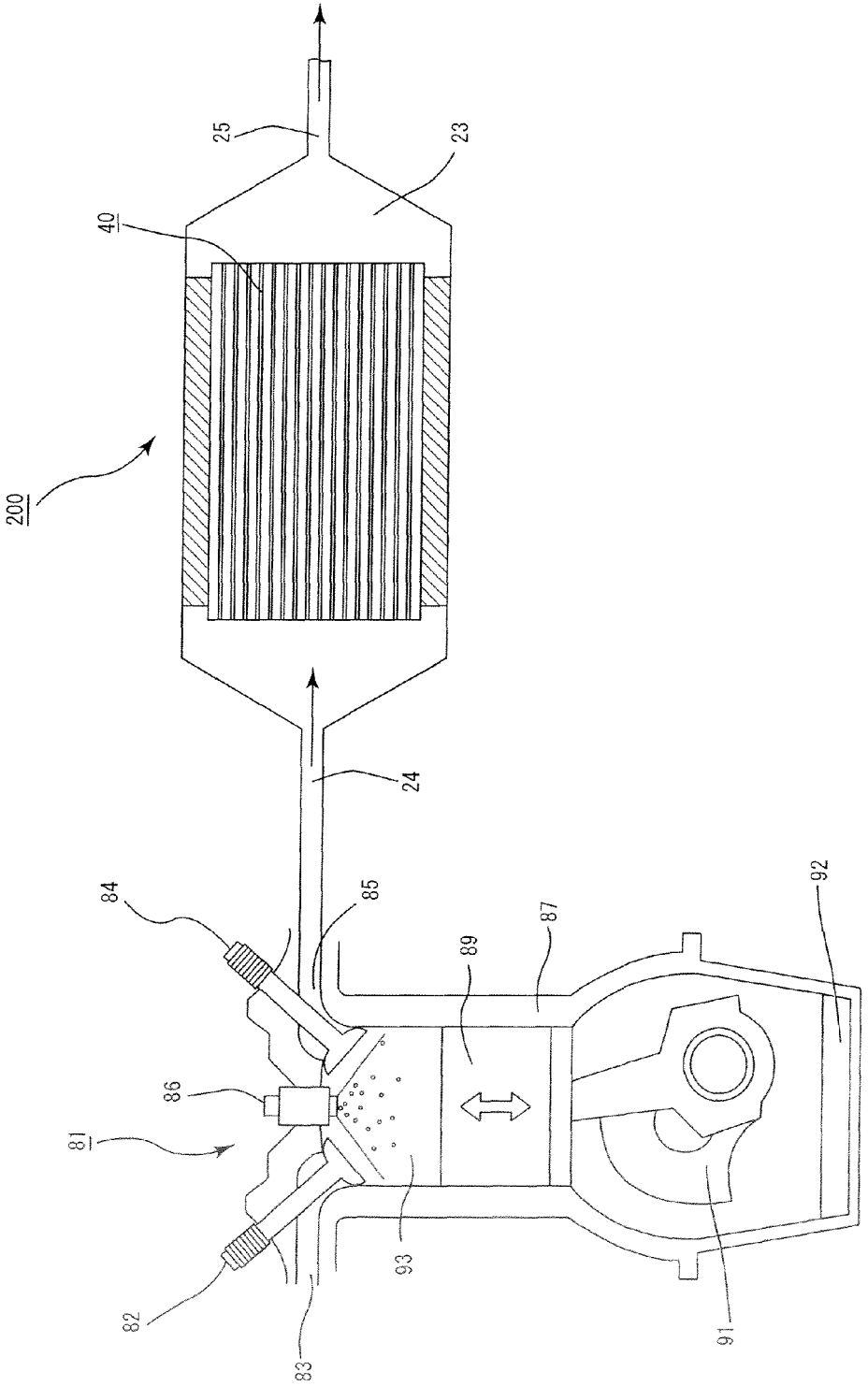


Fig. 2

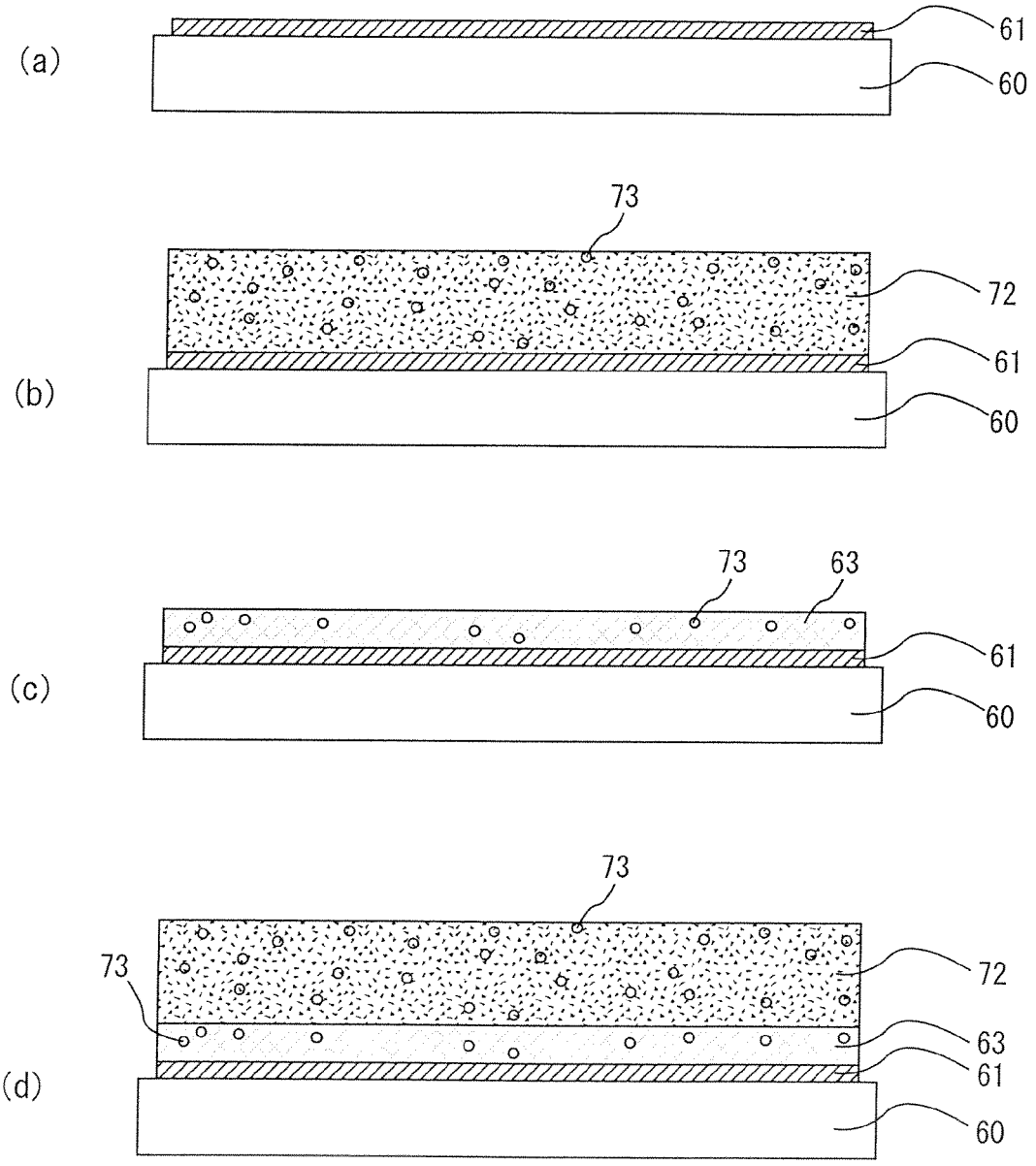


Fig. 3

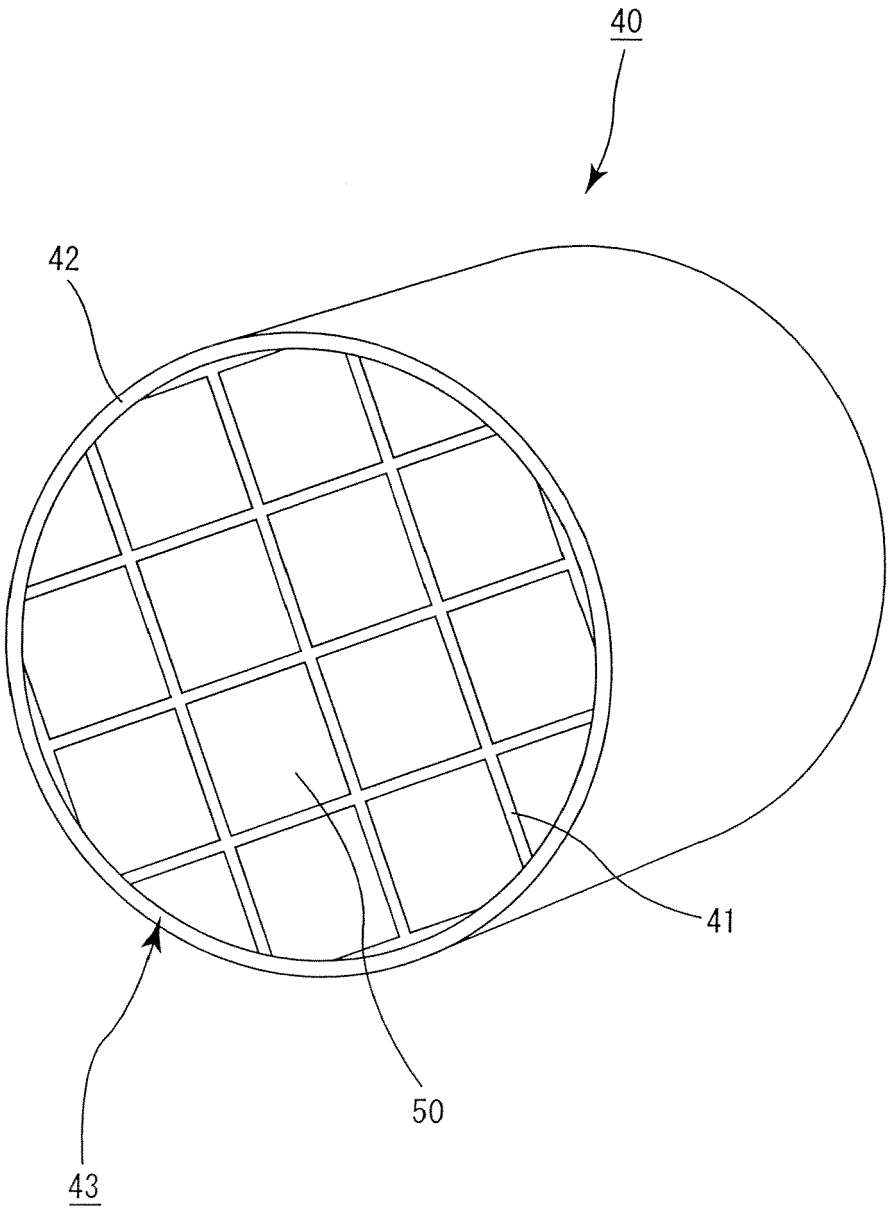
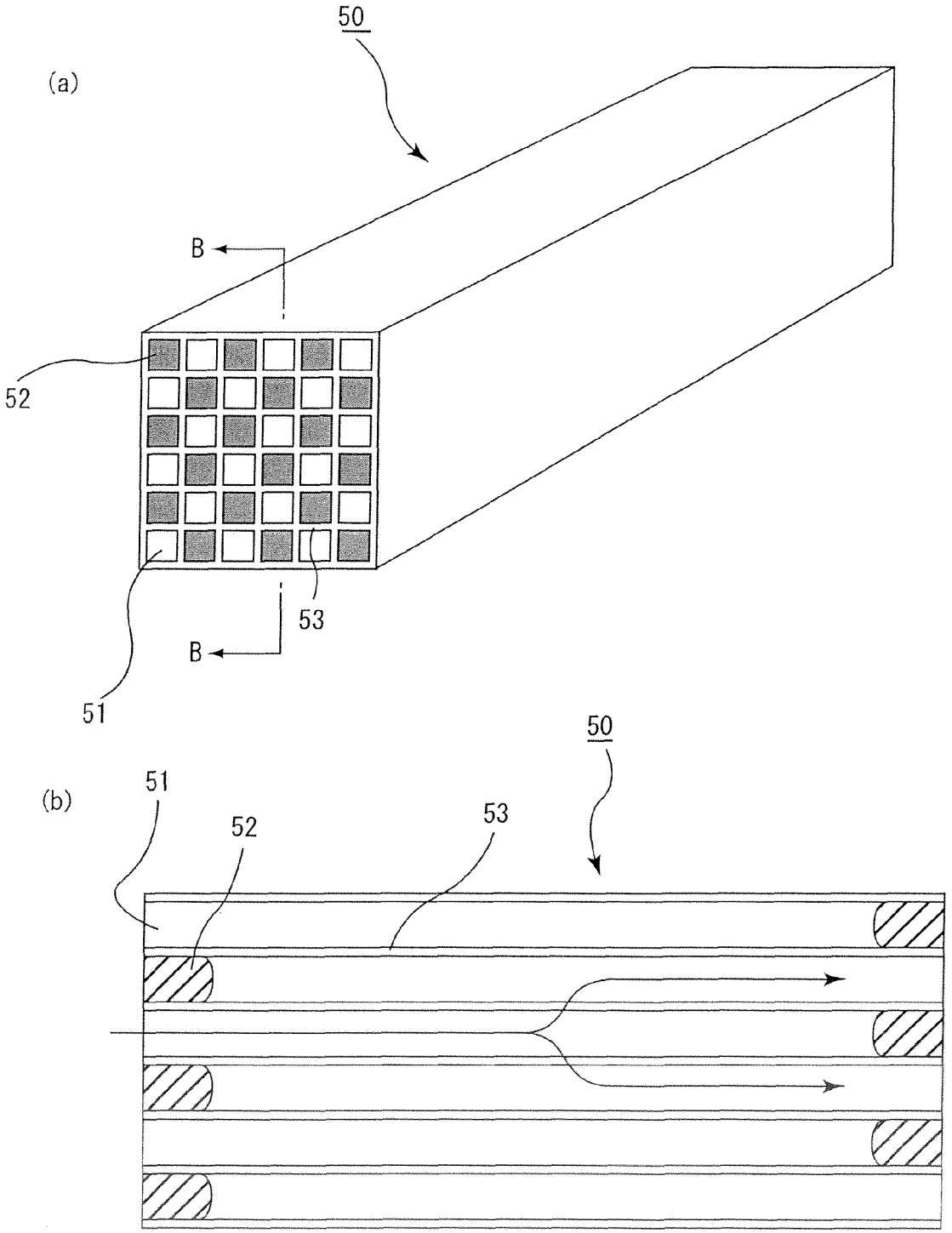


Fig. 4



B-B line cross-sectional view

Fig. 5

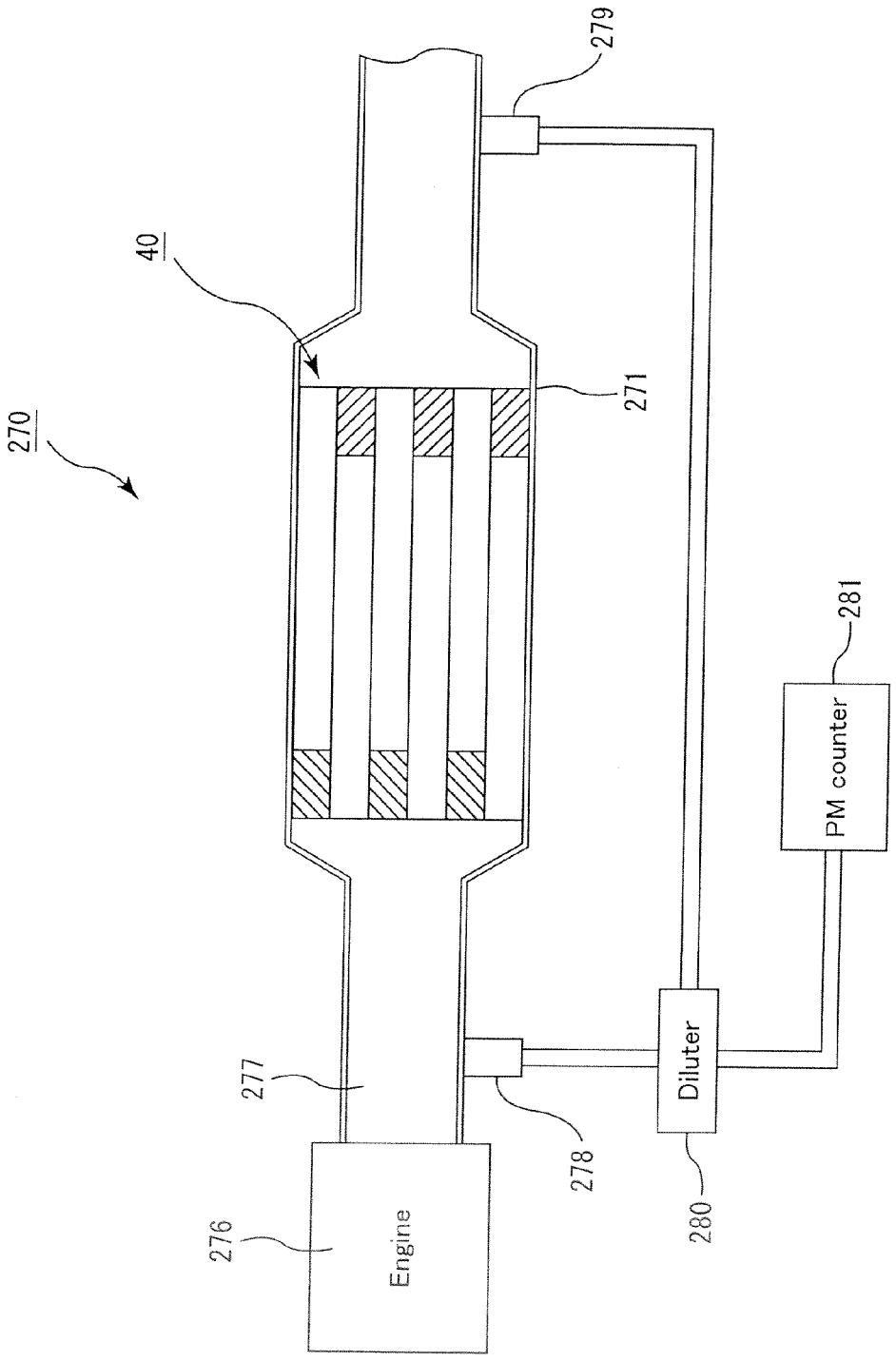
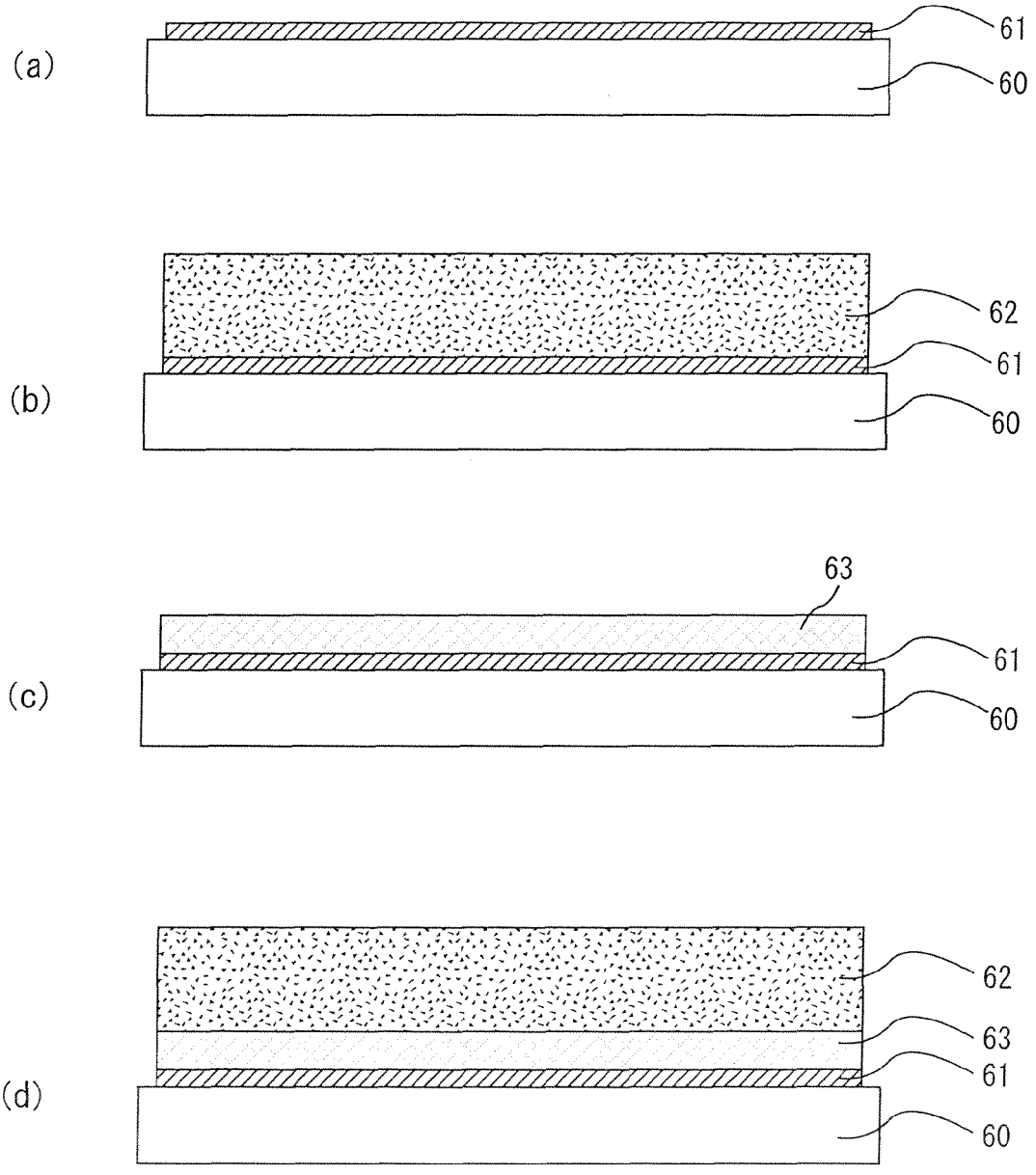


Fig. 6



European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number EP 06 11 4706

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2004/194454 A1 (RIM JULIUS J) 7 October 2004 (2004-10-07) * claims 1,11,13-15 *	1-15	INV. C10M159/18
X	US 5 819 529 A (PETER-HOBLYN ET AL) 13 October 1998 (1998-10-13) * column 8, line 11 - line 23; claim 5; table 3 *	1-15	
X	US 4 946 609 A (PRUESS ET AL) 7 August 1990 (1990-08-07) * claims 1-9 *	1-15	
X	EP 1 416 034 A (INFINEUM INTERNATIONAL LIMITED) 6 May 2004 (2004-05-06) * page 8, paragraph 56 - page 9, paragraph 69 *	1-3,12, 13	
X	US 3 217 022 A (CORDES HANS) 9 November 1965 (1965-11-09) * column 3, line 54 - line 56 *	1-3,8, 12,13	
	-/--		TECHNICAL FIELDS SEARCHED (IPC) C10M

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
Munich	13 September 2006	Klaes, Daphne

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EPO FORM 1503 03.82 (P04C07)



European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 06 11 4706

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US 4 655 949 A (LANDRY ET AL) 7 April 1987 (1987-04-07) * column 6, line 1 - line 5; table V * -----	1-3,12, 13	
X	US 2005/081430 A1 (CARROLL ROBERT W ET AL) 21 April 2005 (2005-04-21) * column 7, paragraph 87; table I * -----	1,2,12	
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 168 (C-0932), 22 April 1992 (1992-04-22) & JP 04 013798 A (TAIHO IND CO LTD), 17 January 1992 (1992-01-17) * abstract * -----	4	TECHNICAL FIELDS SEARCHED (IPC)

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European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 06 11 4706

Claim(s) searched completely:
12-15

Claim(s) searched incompletely:
1-11

Claim(s) not searched:
-

Reason for the limitation of the search:

For the assessment of novelty of a product claim the intended use of the product is not relevant. Therefore, independent claim 1 as drafted discloses any compound containg a metallic element. Therefore, The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claims 1-11 may be said to define subject-matter for which protection might legitimately be sought (Article 84 EPC).

For these reasons, a meaningful search of the whole claimed subject matter of claim 1 and its dependent claims 2-11 could not be carried out (Rule 45 EPC). The extent of the search was consequently limited.

The search of claims 1-11 was restricted to engine oils comprising the additives of said claims.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 11 4706

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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