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(54) **SEGREGATED CATALYZED METALLIC WIRE FILTER FOR DIESEL SOOT FILTRATION**
SEGREGIERTER, KATALYSIERTER METALLDRAHTFILTER ZUR DIESELRUSSFILTRATION
FILTRE A FILS METALLIQUES CATALYSES SEPARÉS POUR FILTRAGE DES SUIES DIESEL

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US-A- 4 573 317 US-A- 5 551 971

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Description

[0001] This invention relates to diesel engine exhaust gas treatment and more particularly to the filtering of particulates from diesel engine exhaust gases using a catalyzed filter.

[0002] Diesel engine exhaust is a heterogeneous mixture which contains not only gaseous emissions such as carbon monoxide ("CO"), unburned hydrocarbons ("HC") and nitrogen oxides ("NOx"), but also condensed phase materials (liquids and solids) which constitute the so-called particulates or particulate matter ("PM"). The total particulate matter ("TPM") emissions are comprised of three main components. One component is the solid, dry, solid carbonaceous fraction or soot. This dry carbonaceous matter contributes to the visible soot emissions commonly associated with diesel exhaust. A second component of the TPM is the soluble organic fraction ("SOF"). The soluble organic fraction is sometimes referred to as the volatile organic fraction ("VOF"), which terminology will be used herein. The VOF may exist in diesel exhaust either as a vapor or as an aerosol (fine droplets of liquid condensate) depending on the temperature of the diesel exhaust, and are generally present as condensed liquids at the standard particulate collection temperature of 52° C in diluted exhaust, as prescribed by a standard measurement test, such as the U.S. Heavy Duty Transient Federal Test Procedure. These liquids arise from two sources: (1) lubricating oil swept from the cylinder walls of the engine each time the pistons go up and down; and (2) unburned or partially burned diesel fuel.

[0003] The third component of the particulates is the so-called sulfate fraction. Diesel fuel contains sulfur, and even the low sulfur fuel available in the U.S. may contain 0.005% sulfur. Upon combustion of the fuel in the engine, nearly all of the sulfur is oxidized to sulfur dioxide which exits with the exhaust in the gas phase. However, a small portion of the sulfur, perhaps 2-5%, is oxidized further to SO₃, which in turn combines rapidly with water in the exhaust to form sulfuric acid which collects as a condensed phase with the particulates as an aerosol, or is adsorbed onto the other particulate components, and thereby adds to the mass of TPM.

[0004] Emissions from diesel engines have been under increasing scrutiny in recent years and standards, especially for particulate emissions, have become stricter. In 1994 the particulate emission standards in the U.S. for new engines allowed no more than a total of 0.1 grams per brake horse power hour (g/BHP-h). For diesel engines in buses operating in congested urban areas the particulate emissions standard was even stricter, 0.07 g/BHP-h TPM. Both of these standards were seen as significant reductions relative to the prior particulate emission standard of 0.25 g/BHP-h which had been in effect since 1991. Starting in 1994, for the first time, engine technology developments alone were found to be incapable of meeting the new standards, and for some

engines after treatment technology, for example, diesel oxidation catalyst (DOC) units, as discussed further below, were necessary.

[0005] The question of how best to reduce the levels of particulate matter expelled to the atmosphere in the exhaust gases of diesel engines is currently of considerable interest as stricter emission standards are constantly being legislated through the next decade. In this connection, it is desired to develop efficient and practical devices for removing substantial portions of particulates from the exhaust gases in diesel engine exhaust systems before permitting the exhaust gases to escape to the atmosphere.

[0006] It is known in the art to provide diesel engines with an exhaust filter which traps particulates from the exhaust gas stream during engine operation. The filters are generally made of porous, solid materials having a plurality of pores extending therethrough and having small cross-sectional size, such that the filter is permeable to the exhaust gases which flow through the filters and are capable of restraining most or all of the particulates from passing through the filter with the gas. The restrained particulates consist generally of carbonaceous particulates in the form of soot particles and reference herein and in the claims to "particulate" and "particulates" means such diesel engine-generated particles. As the mass of collected particulates increases, the flow rate of the exhaust gas through the filter is usually impeded, whereby an increased back pressure is encountered within the filter and reduced engine efficiency results.

[0007] US 4,573,317 A relates to a diesel exhaust cleaner and regeneration system with indexing particulate trap. GB 2 007 994 A, on the other hand, concerns a filter for use in an automotive exhaust system to remove particulate carbon and other solids from hot exhaust gas, wherein said filter contains a mass of wire wool or wire mesh.

[0008] There is a desire in the art to more simply regenerate the particulate filter by continuous burn-off or incineration of the soot particles as they are trapped in the filter. However, experience has shown that in normal diesel engine operation, the temperature in the exhaust system varies substantially under different conditions of engine load and speed and that the temperatures in the filter hardly ever reach the 510° C temperature level required to incinerate the trapped particulate.

[0009] In order to comply with the ever-increasing legislation both in the United States and Europe to reduce the level of solid emissions from both on- and off-highway diesel-powered vehicles, exhaust after-treatment, such as a variety of soot filter media, have been explored. The wallflow type ceramic honeycomb filter is the most widely employed filtration technology used in current systems for industrial applications. Wallflow filters provide an answer to the filtration requirement, yet there remains the residual problem of achieving a reliable and repeatable method of cleaning the filter. This residual problem has

been the source of extensive engineering research and development. Wallflow filter elements are particularly useful to filter particulate matter from diesel engine exhaust gases. Many references disclose the use of wallflow filters which can comprise catalysts on or in the filter to filter and burn off filtered particulate matter. A common ceramic wallflow filter construction is a multichannel honeycomb structure having the ends of alternate channels on the upstream and downstream sides of the honeycomb structure plugged. This results in a checkerboard-type pattern on either end. Channels plugged on the upstream or inlet end are open on the downstream or outlet end. This permits the gas to enter the open upstream channels, flow through the porous walls and exit through the channels having open downstream ends. The gas pressure forces the gas through the porous structural walls into the channels closed at the upstream end and open at the downstream end. Such structures are primarily disclosed to filter particles out of the exhaust gas stream.

[0010] It is desired to remove the particulate matter from the upstream sides of the wallflow filters. One method is to provide a layer of catalyst on the wall to catalyze the ignition of the particulate matter during operation of the filter. There are many U.S. patents disclosing such wallflow structures.

[0011] A particularly useful particulate emission control filter directed for use for diesel exhaust is presented in "3M Diesel Filters for Particulate Emission Control, Designers Guide" published by 3M Ceramic Materials Department, printed 1994 January and hereby incorporated by reference. There is described a ceramic filter comprising ceramic fiber specified to have 62% Al_2O_3 , 24% SiO_2 , and 14% B_2O_3 . The filter specification includes a white continuous fiber having a fiber diameter of 10-12 microns with a fiber density of 2.7 grams per cubic centimeter. The mechanical properties of the fiber include a filament tensile strength of 1.72 GPA, a filament tensile modulus of elasticity of 138 GPA, and elongation of 1.2%. The specified thermal properties are continuous use temperature of 1204° C, short-term use temperature at 1371° C, a lineal shrinkage at 1093° C of 1.25%, a melting point of 1800° C, a thermal expansion coefficient (25-500° C) of $3.0 \times 10^{-6} \Delta\text{L}/\text{L}^\circ \text{C}$, and a specific heat of 1046.7 J/Kg° K. The fiber is sold by the 3M Ceramic Materials Department as NEXTEL™ FIBER. The above specified properties are for NEXTEL™ 312 CERAMIC FIBER.

[0012] The NEXTEL™ fibers are used to make diesel filters. A typical 3M diesel filter cartridge has a cylindrical support and a continuous ceramic fiber woven in a diamond pattern on the support to form a ceramic fiber winding, see U.S. 5,551,971, Figure 1. The cylindrical support is an electric resistant heating element that contains openings. The area of the openings can be used to control the heat input along the support. Where less heat is desired, the support can have larger openings or more openings at a given location. The distribution of openings can be varied with the most open area toward the center

of the support. The cylindrical support has an open end and a closed end. The filter is useful to filter particulate matter from diesel engine exhaust. During engine operation gas laden with particulate matter can pass through the outer circumferential surface of the ceramic fiber windings through the open areas of the cylindrical support and out through the open end. Alternatively and preferably, the filter cartridge can be operated in reverse. Particle laden gases can be fed into open end, pass through the open areas of cylindrical support and then through ceramic fiber windings depositing its particles in the ceramic fiber windings.

[0013] During heating to regenerate the filter, an oxygen laden gas, preferably air, is fed into open end. Electric energy is input to heat the cylindrical support which acts as a heating element or heater. The cylindrical heating element heats the ceramic fiber windings to a temperature sufficient to oxidize particulate matter trapped thereon.

[0014] The filter cartridge is used in a diesel engine exhaust system. Typically, a plurality of filters are assembled within a canister. The number of filter cartridges assembled in a canister is sized to the exhaust flow rates and anticipated regeneration intervals.

[0015] While a variety of soot filters are known in the art, improvements are continually desired not only in the regeneration of such filters, but for the ease of manufacture, retrofitting, and replacement of such filters. Improvements are further desired in maintaining gas flow through the filters even if soot accumulation exceeds the soot-burning rate of the filtering media so as to keep the vehicle running until cleaning can occur.

[0016] A diesel soot filter is provided comprising a plurality of parallel channels that are composed of a metallic mesh to trap soot particles as the diesel exhaust gas passes through the channels. The filtering channels are arranged such as in a canister such that smaller by-pass gas channels are formed between the filtering channels. The by-pass channels allow the exhaust gas to pass therethrough in the event that soot accumulation in the main filtering channels exceeds the burning rate of the accumulated soot. The reduced gas flow through the by-pass channels reduces the back pressure and keeps the vehicle running until a favorable regeneration of the filter is achieved. The wire mesh can be removed from the channels and replaced with new metal mesh, and/or the channels containing the metal mesh may also be removed and replaced if needed to renew soot removal.

Figure 1 is a longitudinal cross-sectional view of a canister holding the soot filter channels of this invention and taken along line 1-1 of Figure 2.

Figure 2 is a transverse sectional view of the canister and soot filter device of the present invention taken along line 2-2 of Figure 1.

Figure 3 is a perspective view of a soot filter channel of this invention.

Figure 4 is a plan view of one of the end plates which

can be used to hold the soot filter channels in place.

[0017] In Fig. 1, the filtering element of this invention is shown installed as a diesel particulate trap 10 which has a canister of rectangular tubular casing 12, a pyramidal exhaust inlet 14, and a pyramidal exhaust outlet 16. As installed, a plurality of hollow channels 18 extend in the axial or longitudinal direction of the filtering element which is also the primary direction of the flow of exhaust through the diesel particulate trap. The metal sleeve 20 of the filtering element has been sealed to the casing 12 by an intumescent mat 24 that expands when exposed to the heat of the first use of the diesel particulate trap. Any such mat should be selected to withstand temperatures encountered in use, especially temperatures at which the filtering element is to be regenerated. A particularly useful intumescent mat is provided by a heat-expandable vermiculite mat.

[0018] The channel walls which form each of channels 18 are impervious metal sheet in circular, square, trapezoid, rectangular, etc., designs shown in Figs. 1 and 2 as cylindrical channels 18 having a circular cross-section and open at each end 19 and 21. The inside diameter of channel 18, regardless of shape, will be at least 0.5 in, preferably at least about 1.0 inch wide. A plurality of channels 18 are placed within enclosed area 26 of casing 12. End plates 23 and 25 on opposite ends of area 26 and welded or otherwise attached to metal sleeve 20 support the opposing ends of channels 18. End plates 23 and 25 can include openings through which the ends of channels 18 are supported. The channels 18 may be permanently fixed to end plates 23 and 25 or temporarily fit so that such channels can be replaced due to wear. Thus, the outside diameters or perimeters of channels 18 can be such as to be pressure fit within the openings 32 of the end plates 23 and 25, see Fig. 4, or otherwise removably attached thereto such by bolts, screws, etc., so as to remain in place during use. Upon wear, the channels 18 can be removed from the respective openings 32 in the end plates 23 and 25 and slid from the interior of enclosed area 26 for repair and/or replacement.

[0019] Within the interior of each channel 18 is placed a metal mesh filtering element 28 which is capable of trapping the soot particles contained within the diesel exhaust. The metal mesh can be of various types and configurations so long as the mesh filtering element 28 allows for gas flow therethrough, but forms a barrier for soot particles. Woven metal mesh such as of steel wool type, non-woven wire mesh in which individual wires are spot soldered or the like with other wires to form a single mesh unit, braided wire mesh in which a plurality of wire strands are twisted together to form a mesh capable of the desired removal of soot from a passing gas stream can be used. The metal mesh filtering element 28 is preferably placed as a single mass within the interior of each channel 18 so as to substantially completely fill the channel interior. More than one piece of metal mesh can be used if more convenient to fill the channel interiors. The metal

mesh filtering element 28 can be readily removable from within each channel 18 so as to be easily substituted with repaired, regenerated, or a new mesh element to maintain optimum filtering capability. The metal mesh filtering element 28 can be pressure fit within each channel interior so as to remain in place during operation. Alternatively, or in addition to pressure fitting, each open end 19 and 21 of channel 18 may contain one or more cross pieces or mesh (not shown) to keep the metal mesh filtering element 28 in place within the interior of channels 18.

[0020] It is well known in the art of diesel soot filters to burn off the soot particles from the filter so as to regenerate the filter and again improve its capacity to filter the soot particles from the exhaust gas. Unfortunately, the temperature generated by the diesel engine and imparted to the exhaust gas is not high enough to initiate ignition and burning of the soot particles. Accordingly, oxidation catalysts have been incorporated onto the filtering element so as to lower the ignition temperature of the soot particles and allow the particles to be burned and the filter element regenerated either on a continuous or alternating process between filtering and regenerating. In accordance with the present invention, the metal mesh elements 28 of this invention can be coated with the oxidation catalysts well known in the art to initiate the ignition of the soot particles from the diesel exhaust gas that are trapped within the filtering element. The types of catalysts and the methods of applying the catalysts to the metal mesh filtering element 28 are more fully explained below. In addition to coating the wire mesh filtering element 28, it is also possible to coat the interior of the channels 18 with an oxidation catalyst to initiate ignition of any soot particles attached to the interior walls and/or initiate oxidation of gaseous contaminants within the exhaust gas itself, such as CO, HC, and NOx. The catalyst on the metal mesh filtering element 28 may be the same or different than the catalyst that is coated on the interior walls of channels 18. Further, any wire elements used to maintain the filtering elements 28 in place within channels 18, such as any mesh or the like, provided in openings 19 and 21 can also be provided with a catalytic coating. Still further, it may be possible to provide an oxidation catalyst on at least a portion of the exterior of the channels 18, in particular, those areas of the channels which are in contact with the interstitial voids 30, which are formed between the channels 18 as the channels are stacked within enclosed area 26 of casing 12. Thus, exhaust gas that passes through the interstitial voids 30 can be treated so as to initiate oxidation of the exhaust gas contaminants.

[0021] The filter device 10 of this invention will be placed in an exhaust stream from a diesel engine. A diesel oxidation catalyst (DOC) may or may not be placed in front of the filtering device 10 dependent upon the application. An exhaust gas from the diesel engine containing HC, CO, NOx, and particulate matter passes through the filter device 10 and, in particular, channels 18. Due to the impaction of the soot particles on the catalyzed

wire mesh element 28, the soot particles are collected and burnt under suitable exhaust regeneration conditions. If the application is such that the soot accumulation rate on filter element 28 exceeds the burning rate of the soot particles, exhaust gas flow from the engine will be forced and diverted through the interstices 30 between the stacked channels 18 within casing 12. The interstitial voids 30 are initially sized to permit only minor flow during most diesel engine operating conditions since the back pressure in the interstices 30 is higher than the back pressure through mesh filtering element 28. Typically the interstitial void volume within enclosed area 26 of casing 12 will comprise less than 25% of the volume of enclosed area 26. Gas flow through the interstitial void volume can be controlled or limited by use of orifice openings 34 in the endplates such as shown for endplate 23 in Fig.4. When the soot accumulates and starts to block the pores of the metal mesh filtering element 28 and the back pressure rises, the interstitial or bypass voids 30 still enable exhaust gas flow and allow the diesel engine to continue operation. In this way the vehicle will not stall due to a totally restricted flow path of the exhaust gas. The density of the wire mesh (wire diameter and the amount of wire weaved into the matrix) determines the back pressure.

[0022] The metal mesh can be made of any relatively high temperature alloy, including most stainless steels, FeCrAlloy, Hastalloy, etc.

[0023] In a preferred embodiment of the invention, the metal mesh is pretreated prior to deposition of the catalyst composition to improve the adherence of composition on the substrate. Pretreatment of the substrate can be conducted by applying a metal anchor layer to the substrate by known thermal spraying techniques before the catalyst slurry is applied. These techniques include plasma spraying, single wire spraying, high velocity oxy-fuel spraying, combustion wire and/or powder spraying, electric arc spraying etc. Preferably the metal anchor layer is applied by electric arc spraying.

[0024] Electric arc spraying, e.g., twin wire arc spraying, of a metal (which term, as used herein, includes mixtures of metals, including without limitation, metal alloys, pseudoalloys, and other intermetallic combinations) onto a metal foraminous substrate yields a structure having superior utility as a substrate for catalytic materials in the field of catalyst members. Twin wire arc spraying (encompassed herein by the term "wire arc spraying" and by the broader term "electric arc spraying") is a known process, disclosed in United States Patent No. 4,027,367 which is incorporated herein by reference. Briefly described, in the twin wire arc spray process, two feedstock wires act as two consumable electrodes. These wires are insulated from each other as they are fed to the spray nozzle of a spray gun in a fashion similar to wire flame guns. The wires meet in the center of a gas stream generated in the nozzle. An electric arc is initiated between the wires, and the current flowing through the wires causes their tips to melt. A compressed atomizing gas, usually air, is directed through the nozzle and across the arc

zone, shearing off the molten droplets to form a spray that is propelled onto the substrate. Only metal wire feedstock can be used in an arc spray system because the feedstock must be conductive. The high particle temperatures created by the spray gun produce minute weld zones at the impact point on a metallic substrate. As a result, such electric arc spray coatings (sometimes referred to herein as "anchor layers") maintain a strong adhesive bond with the substrate.

[0025] Operating parameters for wire arc spraying for forming anchor layer on foraminous substrates are disclosed in copending United States Patent Application No. 09/301,626, filed April 29, 1999 (the '626 application), now U.S. Publication No. 2002/0128151, published September 12, 2002, the disclosure of which is hereby incorporated by reference in its entirety.

[0026] Anchor layers of a variety of compositions can be deposited on a substrate by utilizing, without limitation, feedstocks of the following metals and metal mixtures: Ni, Ni/Al, Ni/Cr, Ni/Cr/AUy, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 and 400 series stainless steels, and, optionally, mixtures of one or more thereof. One specific example of a metal useful for wire arc spraying onto a substrate in accordance with the '626 application is a nickel/aluminum alloy that generally contains at least about 90% nickel and from about 3% to 10% aluminum, preferably from about 4% to 6% aluminum by weight. Such an alloy may contain minor proportions of other metals referred to herein as "impurities" totaling not more than about 2% of the alloy. A preferred specific feedstock alloy comprises about 95% nickel and 5% aluminum and may have a melting point of about 2642 °F. Some such impurities may be included in the alloy for various purposes, e.g., as processing aids to facilitate the wire arc spraying process or the formation of the anchor layer, or to provide the anchor layer with favorable properties.

[0027] Electric arc spraying a metal onto a metal substrate yields a superior substrate for catalytic materials relative to substrates having metal anchor layers applied thereto by other methods. Catalytic materials have been seen to adhere better to a substrate comprising an electric arc sprayed anchor layers than to a substrate without an intermediate layer applied thereto and even better than to a substrate having a metal layer deposited thereon by plasma spraying. Catalytic materials disposed on metal substrates, without intermediate layers between the substrate and the catalytic material, often did not adhere sufficiently well to the substrate to provide a commercially acceptable product. Metal substrates having an intermediate layer applied by other thermal spraying techniques typically suffer the same drawbacks. For example, a metal substrate having a metal intermediate layer that was plasma-sprayed thereon and having a catalytic material applied to the intermediate layer failed to retain the catalytic material, which flaked off upon routine handling, apparently due to a failure of the intermediate layer to bond with the substrate. The catalytic material

on other substrates was seen to spall off upon normal use, apparently as a result of being subjected to a high gas flow rate, to thermal cycling, to the eroding contact of high temperature steam and other components of the exhaust gas stream, vibrations, etc. Application of the intermediate layer by electric arc spraying therefore improves the durability of catalyst members comprising catalytic materials carried on foraminous substrates by improving their durability.

[0028] The metal mesh filter elements of this invention (also referred to herein as foraminous substrates) useful for forming the filtering elements include those metallic substrates which are able to accommodate a high flow rate, are lightweight and have a low thermal mass. The woven, non-woven, and braided wire mesh of this invention as filter element 28 are suitable for application of a metal anchor layer.

[0029] A suitable catalytic material for use on a foraminous substrate can be prepared by dispersing a compound and/or complex of any catalytically active component, e.g., one or more platinum group metal compounds or complexes, onto relatively inert bulk support material. As used herein, the term "compound", as in "platinum group metal compound" means any salt, complex, or the like of a catalytically active component (or "catalytic component") which, upon calcination or upon use of the catalyst, decomposes or otherwise converts to a catalytically active form, which is often, but not necessarily, an oxide. The compounds or complexes of one or more catalytic compounds may be dissolved or suspended in any liquid which will wet or impregnate the support material, which does not adversely react with other components of the catalytic material and which is capable of being removed from the catalyst by volatilization or decomposition upon heating and/or the application of a vacuum. Generally, both from the point of view of economics and environmental aspects, aqueous solutions of soluble compounds or complexes are preferred. For example, suitable water-soluble platinum group metal compounds are chloroplatinic acid, amine solubilized platinum hydroxide, rhodium chloride, rhodium nitrate, hexamine rhodium chloride, palladium nitrate or palladium chloride, etc. The compound-containing liquid is impregnated into the pores of the bulk support particles of the catalyst, and the impregnated material is dried and preferably calcined to remove the liquid and bind the platinum group metal into the support material. In some cases, the completion of removal of the liquid (which may be present as, e.g., water of crystallization) may not occur until the catalyst is placed into use and subjected to the high temperature exhaust gas. During the calcination step, or at least during the initial phase of use of the catalyst, such compounds are converted into a catalytically active form of the platinum group metal or a compound thereof. An analogous approach can be taken to incorporate the other components into the catalytic material. Optionally, the inert support materials may be omitted and the catalytic material may consist essentially of the catalytic compo-

nent deposited directly on the sprayed foraminous substrate by conventional methods.

[0030] Preferred platinum group metal components for use in the articles of the invention include platinum, palladium, rhodium, ruthenium and iridium components. Platinum, palladium and rhodium components are particularly preferred. When deposited on a foraminous substrate (e.g., metal screen) such components are generally deposited at a concentration of from 0.001 to 0.01 g/in² for typical utility engine applications.

[0031] Suitable support materials for the catalytic component include alumina, silica, titania, silica-alumina, aluminosilicates, aluminum-zirconium oxide, aluminum-chromium oxide, etc. Such materials are preferably used in their high surface area forms. For example, gamma-alumina is preferred over alpha-alumina. It is known to stabilize high surface area support materials by impregnating the material with a stabilizer species. For example, gamma-alumina can be stabilized against thermal degradation by impregnating the material with a solution of a cerium compound and then calcining the impregnated material to remove the solvent and convert the cerium compound to a cerium oxide. The stabilizing species may be present in an amount of from about, e.g., 5 percent by weight of the support material. The catalytic materials are typically used in particulate form with particles in the micron-sized range, e.g., 10 to 20 microns in diameter, so that they can be formed into a slurry and coated onto a substrate.

[0032] A typical catalytic material for use on a filter member for diesel engine exhaust comprises platinum, palladium and rhodium dispersed on an alumina and further comprises oxides of neodymium, strontium, lanthanum, barium and zirconium. Some suitable catalysts are described in United States Patent Application Serial. No. 08/761,544 filed December 6, 1996, the disclosure of which is incorporated herein by reference. In one embodiment described therein, a catalytic material comprises a first refractory component and at least one first platinum group component, preferably a first palladium component and optionally, at least one first platinum group metal component other than palladium, an oxygen storage component which is preferably in intimate contact with the platinum group metal component in the first layer. An oxygen storage component ("OSC") effectively absorbs excess oxygen during periods of lean engine operation and releases oxygen during periods where localized concatenations of fuel produce a rich environment as seen in light-off of the catalyst after prolonged idle condition. Bulk ceria is known for use as a OSC, but other rare earth oxides may be used as well. In addition, as indicated above, a co-formed rare earth oxide-zirconia may be employed as a OSC. The co-formed rare earth oxide-zirconia may be made by any suitable technique such as co-precipitation, co-gelling or the like. One suitable technique for making a co-formed ceria-zirconia material is illustrated in the article by Luccini, E., Mariani, S., and Sbaizero, O. (1989) "Preparation of Zirconia Ce-

rium Carbonate in Water With Urea" Int. J. of Materials and Product Technology, vol. 4, no. 2, pp. 167-175, the disclosure of which is incorporated herein by reference. As disclosed starting at page 169 of the article, a dilute (0.1 M) distilled water solution of zirconyl chloride and cerium nitrate in proportions to promote a final product of ZrO_2 -10 mol % CeO_2 is prepared with ammonium nitrate as a buffer, to control pH. The solution was boiled with constant stirring for two hours and complete precipitation was attained with the pH not exceeding 6.5 at any stage.

[0033] Any suitable technique for preparing the co-formed rare earth oxide-zirconia may be employed, provided that the resultant product contains the rare earth oxide dispersed substantially throughout the entire zirconia matrix in the finished product, and not merely on the surface of the zirconia particles or only within a surface layer, thereby leaving a substantial core of the zirconia matrix without rare earth oxide dispersed therein. Thus, co-precipitated zirconium and cerium (or one other rare earth metal) salts may include chlorides, sulfates, nitrates, acetates, etc. The co-precipitates may, after washing, be spray dried or freeze dried to remove water and then calcined in air at about 500 °C. to form the co-formed rare earth oxide-zirconia support. The catalytic materials of aforesaid application serial. No. 08/761,544 may also include a first zirconium component, at least one first alkaline earth metal component, and at least one first rare earth metal component selected from the group consisting of lanthanum metal components and neodymium metal components. The catalytic material may also contain at least one alkaline earth metal component and at least one rare earth component and, optionally, at least one additional platinum group metal component preferably selected from the group consisting of platinum, rhodium, ruthenium, and iridium components with preferred additional first layer platinum group metal components being selected from the group consisting of platinum and rhodium and mixtures thereof.

[0034] A variety of deposition methods are known in the art for depositing catalytic material on a foraminous substrate. These methods of applying the catalytic component onto the substrate constitute a separate step in the manufacturing process relative to the application of any anchor layer (if applied) to the substrate.

[0035] Methods for depositing catalytic material on the foraminous substrate include, for example, disposing the catalytic material in a liquid vehicle to form a slurry and wetting the foraminous substrate with the slurry by dipping the substrate into the slurry, spraying the slurry onto the substrate, etc. Alternatively, the catalytic material may be dissolved in a solvent and the solvent may then be wetted onto the surface of the foraminous substrate and thereafter removed to leave the catalytic material, or a precursor thereof, on the foraminous substrate. The removal procedure may entail heating the wetted substrate and/or subjecting the wetted substrate to a vacuum to remove the solvent via evaporation.

Example 1 Preparation of a Catalyst Composition Containing Platinum and Palladium in a 4:1 Ratio

[0036] First platinum and palladium compounds were dispersed on high surface area gamma alumina and 5% lanthanum modified alumina supports. Into 2104.5 g of gamma alumina (97% solids) and 2041 g of 5% lanthanum stabilized alumina was added an aqueous solution containing 133.9 g of Pt as a 16% amine solubilized platinum hydroxide diluted with 709 g of deionized water with mixing. After mixing for additional 20 minutes a Pd solution was added containing 33.5 g Pd as a 19% palladium nitrate solution diluted with 700 g of deionized water. This was mixed an additional 20 minutes to ensure the powder was uniformly contacted with the precious metal solution.

[0037] The resulting precious metal support mixture from above was contacted with 6189 g of deionized water, 433.9 g of 90 acetic acid and 18 g of octanol in a dispersion tank. This mixture was fed into a continuous mill and ground until > 90% of the material had a particle diameter of less than 5 microns. A Ce/Zr composite oxide was added with an additional 120 g of acetic acid and the resulting slurry was further ground until the overall particle size was 90% < 1 micron. In a dispersion tank 583.3 g of zirconyl acetate solution was added to the slurry and mixed vigorously. The final pH of the slurry was in the range of 4.0-4.8.

Example 2 - Preparation of Wire Mesh Foraminous Catalytic Substrate

[0038] To prepare an article having the design as shown in Figure 1, a stainless steel wool mesh was wire arc spray-coated with a nickel-aluminide alloy as described in Example 1 of the aforesaid '626 application. The steel wool mesh was then coated with the coating slurry described above (Example 1) at a washcoat loading of 0.05 to 0.1 g/in². The mesh was then fitted into a cylindrical channel having an inside diameter of 1.25 in.

[0039] While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations in the preferred devices and methods may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the claims that follow.

Claims

1. A filter (10) for removing soot particles from the exhaust of a diesel engine comprising:

an enclosed area (26),
a plurality of channels (18) disposed within said enclosed area and disposed longitudinally in the

- same direction as gas flow through the filter, each of said channels having a hollow interior and containing opposed open ends, disposed within each of said channels and substantially filling said hollow interior is an optionally removable metal mesh (28),
said filter including a void space (30) between said plurality of channels, said void space being open to said exhaust.
2. The filter of claim 1, wherein the volume of said void space is less than 25% of the volume of said enclosed area.
 3. The filter of claim 1, wherein said metal mesh is a woven metal mesh or a non-woven metal mesh.
 4. The filter of claim 1, wherein said metal mesh contained in said channels is of a single mass.
 5. The filter of claim 1, wherein said channels are hollow cylinders.
 6. The filter of claim 1, wherein said metal mesh is coated with an oxidation catalyst.
 7. The filter of claim 6, wherein said oxidation catalyst is a platinum group metal.
 8. The filter of claim 6, containing a metal anchor coat disposed between said metal mesh and said catalyst.
 9. The filter of claim 8, wherein said anchor coat is applied by electric arc spraying.
 10. The filter of claim 6, wherein at least a portion of the interior surfaces of said channels are coated with an oxidation catalyst.
 11. The filter of claim 1, wherein said void space is defined by a plurality of void spaces between each of said channels.
 12. The filter of claim 11, wherein said channels are supported by opposed upstream and downstream end plates (23) and (25), said endplates containing a plurality of orifices (34) to direct exhaust gas to said plurality of void spaces.
 13. A method of removing soot from the exhaust gas of a diesel engine comprising directing said exhaust gas through a diesel filter (10) comprising an enclosed area (26), a plurality of channels (18) disposed within said enclosed area and disposed longitudinally in the same direction as gas flow through the filter, each of said channels having a hollow interior and containing opposed open ends, disposed within each of said channels and substantially filling said hollow interior is an optionally removable metal mesh (28), whereby soot particles contained in said exhaust gas are trapped on said metal mesh, wherein said filter further includes a void space (30) between said plurality of channels, said void space being open to said exhaust gas flow.
14. The method of claim 13, comprising:
 - flowing the exhaust gas to an end plate (23), the end plate in fluid communication with the plurality of channels having a hollow interior and supported by the end plate and with the void space defined between said plurality of channels; filtering soot particles from the exhaust gas by flowing a portion of the gas through the optionally removable metal mesh in the hollow interior of the channel;
 - flowing a portion of the exhaust gas through the void space, the void having no mesh contained therein; and
 - diverting a larger portion of the exhaust gas to the void space as the accumulation of soot particles in the metal mesh increases.
 15. The method of claim 14, further comprising controlling the amount of exhaust gas flowing through the void space by incorporating one or more orifice openings (34) in the end plate.
 16. The method of claim 15, further comprising lowering the ignition temperature of the soot particles filtered in the channels by incorporation of an oxidation catalyst onto the filtering element.
 17. The method of claim 16, further comprising burning off the soot particles filtered in the channels.
 18. The method of claim 14, further comprising oxidizing the portion of the exhaust gas flowing through the void space by providing an oxidation catalyst on at least a portion of the exterior of the channels.
- Patentansprüche**
1. Filter (10) zum Entfernen von Rußpartikeln aus dem Auspuff eines Dieselmotors, umfassend:
 - einen eingeschlossenen Bereich (26);
 - eine Vielzahl von Kanälen (18), die innerhalb des eingeschlossenen Bereichs angeordnet sind und in Längsrichtung in der gleichen Richtung wie der Gasstrom durch den Filter angeordnet sind, wobei jeder der Kanäle einen hohlen Innenraum aufweist und gegenüber liegende offene Enden enthält, wobei ein gegeben-

- falls entfernbare Drahtgeflecht (28) innerhalb jedem der Kanäle angeordnet ist und im Wesentlichen den hohlen Innenraum ausfüllt;
- wobei der Filter einen Hohlraum (30) zwischen der Vielzahl von Kanälen einschließt, wobei der Hohlraum zu dem Auspuff hin offen ist.
2. Filter gemäß Anspruch 1, wobei das Volumen des Hohlraums weniger als 25 % des Volumens des eingeschlossenen Bereichs ausmacht. 5
 3. Filter gemäß Anspruch 1, wobei das Drahtgeflecht ein gewebtes Drahtgeflecht oder ein nicht-gewebtes Drahtgeflecht ist. 10
 4. Filter gemäß Anspruch 1, wobei das in den Kanälen enthaltene Drahtgeflecht aus einer Einzelmasse besteht. 15
 5. Filter gemäß Anspruch 1, wobei die Kanäle Hohlzylinder sind. 20
 6. Filter gemäß Anspruch 1, wobei das Drahtgeflecht mit einem Oxidationskatalysator beschichtet ist. 25
 7. Filter gemäß Anspruch 6, wobei der Oxidationskatalysator ein Metall der Platingruppe ist. 30
 8. Filter gemäß Anspruch 6, enthaltend eine Metallankerbeschichtung, die zwischen dem Drahtgeflecht und dem Katalysator vorgesehen ist. 35
 9. Filter gemäß Anspruch 8, wobei die Ankerbeschichtung durch elektrisches Lichtbogenspritzen aufgebracht wird. 40
 10. Filter gemäß Anspruch 6, wobei mindestens ein Teil der inneren Oberflächen der Kanäle mit einem Oxidationskatalysator beschichtet ist. 45
 11. Filter gemäß Anspruch 1, wobei der Hohlraum durch eine Vielzahl von Hohlräumen zwischen jedem der Kanäle definiert wird. 50
 12. Filter gemäß Anspruch 11, wobei die Kanäle von einander gegenüberliegenden, stromaufwärts und stromabwärts angeordneten Endplatten (23) und (25) getragen werden, wobei die Endplatten eine Vielzahl von Austrittsöffnungen (34) enthalten, um Abgas zu der Vielzahl von Hohlräumen zu leiten. 55
 13. Verfahren zum Entfernen von Ruß aus dem Abgas eines Dieselmotors, umfassend das Leiten des Abgases durch einen Dieselfilter (10), umfassend einen eingeschlossenen Bereich (26), eine Vielzahl von Kanälen (18), die innerhalb des eingeschlossenen Bereichs angeordnet sind und in Längsrichtung in der gleichen Richtung wie der Gasstrom durch den Filter angeordnet sind, wobei jeder der Kanäle einen hohlen Innenraum aufweist und einander gegenüberliegende offene Enden enthält, wobei ein gegebenenfalls entfernbare Drahtgeflecht (28) innerhalb jedem der Kanäle angeordnet ist und im Wesentlichen den hohlen Innenraum ausfüllt, wodurch in dem Abgas enthaltene Rußpartikel auf dem Drahtgeflecht eingefangen werden, wobei der Filter weiter einen Hohlraum (30) zwischen der Vielzahl von Kanälen einschließt, wobei der Hohlraum zu dem Abgasstrom hin offen ist.
 14. Verfahren gemäß Anspruch 13, umfassend:
 - Strömenlassen des Abgases zu einer Endplatte (23), wobei die Endplatte, die mit der Vielzahl an Kanälen mit einem hohlen Innenraum in Fluidverbindung steht und die von der Endplatte getragen werden und wobei der Hohlraum zwischen der Vielzahl an Kanälen definiert ist;
 - Filterieren von Rußpartikeln aus dem Abgas durch Strömenlassen eines Teils des Gases durch das gegebenenfalls entfernbare Drahtgeflecht im hohlen Innenraum des Kanals;
 - Strömenlassen eines Teils des Abgases durch den Hohlraum, wobei der Hohlraum kein darin enthaltenes Geflecht aufweist; und
 - Umleiten eines größeren Teils des Abgases in den Hohlraum in dem Maße, wie die Anhäufung von Rußpartikeln in dem Metallgeflecht zunimmt.
 15. Verfahren gemäß Anspruch 14, weiterhin umfassend das Regulieren der durch den Hohlraum strömenden Abgasmenge durch Einbringen von einer oder mehreren Austrittsöffnungen (34) in der Endplatte.
 16. Verfahren gemäß Anspruch 15, weiterhin umfassend das Absenken der Entzündungstemperatur der in den Kanälen filtrierte Rußpartikel durch Einbringen eines Oxidationskatalysators auf dem Filterelement.
 17. Verfahren gemäß Anspruch 16, weiterhin umfassend das Abbrennen der in den Kanälen filtrierte Rußpartikel.
 18. Verfahren gemäß Anspruch 14, weiterhin umfassend das Oxidieren des Teils des Abgases, welcher durch den Hohlraum strömt, durch Vorsehen eines Oxidationskatalysators auf mindestens einem Teil der Außenseite der Kanäle.

Revendications

1. Filtre (10) pour éliminer des particules de suie de l'échappement d'un moteur diesel comprenant :
 - un espace clos (26)
 - une pluralité de canaux (18) disposés dans ledit espace clos et disposés longitudinalement dans la même direction que l'écoulement gazeux au travers du filtre, chacun desdits canaux possédant un intérieur creux et contenant des extrémités ouvertes opposées, un treillis mécanique (28) éventuellement amovible étant disposé dans chacun desdits canaux et remplissant considérablement ledit intérieur creux,
 - ledit filtre comprenant un espace vide (30) entre ladite pluralité de canaux, ledit espace vide étant ouvert audit échappement.
2. Filtre selon la revendication 1, dans lequel le volume dudit espace vide représente moins de 25 % du volume dudit espace clos.
3. Filtre selon la revendication 1, dans lequel ledit treillis métallique est un treillis métallique tissé ou un treillis métallique non tissé.
4. Filtre selon la revendication 1, dans lequel ledit treillis métallique contenu dans lesdits canaux est d'une masse unique.
5. Filtre selon la revendication 1, dans lequel lesdits canaux sont des cylindres creux.
6. Filtre selon la revendication 1, dans lequel ledit treillis métallique est recouvert d'un catalyseur d'oxydation.
7. Filtre selon la revendication 6, dans lequel ledit catalyseur d'oxydation est un métal du groupe du platine.
8. Filtre selon la revendication 6, qui contient un recouvrement d'ancrage métallique disposé entre ledit treillis métallique et ledit catalyseur.
9. Filtre selon la revendication 8, dans lequel ledit revêtement d'ancrage est appliqué par projection à l'arc électrique.
10. Filtre selon la revendication 6, dans lequel au moins une partie des surfaces intérieures desdits canaux est recouverte d'un catalyseur d'oxydation.
11. Filtre selon la revendication 1, dans lequel ledit espace vide est défini par une pluralité d'espaces vides entre chacun desdits canaux.
12. Filtre selon la revendication 11, dans lequel lesdits canaux sont supportés par des plaques d'extrémité opposées en amont et en aval (23) et (25), lesdites plaques d'extrémité contenant une pluralité d'orifices (34) pour diriger les gaz d'échappement vers ladite pluralité d'espaces vides.
13. Procédé d'élimination de la suie des gaz d'échappement d'un moteur diesel qui consiste à diriger lesdits gaz d'échappement au travers d'un filtre diesel (10) comprenant un espace clos (26), une pluralité de canaux (18) disposés dans ledit espace clos et disposés longitudinalement dans la même direction que l'écoulement gazeux au travers du filtre, chacun desdits canaux possédant un intérieur creux et contenant des extrémités ouvertes opposées, un treillis mécanique (28) éventuellement amovible étant disposé dans chacun desdits canaux et remplissant considérablement ledit intérieur creux, par lequel les particules de suie contenues dans lesdits gaz d'échappement sont retenues sur ledit treillis métallique, dans lequel ledit filtre comprend en outre un espace vide (30) entre ladite pluralité de canaux, ledit espace vide étant ouvert audit écoulement des gaz d'échappement.
14. Procédé selon la revendication 13, comprenant :
 - l'écoulement des gaz d'échappement vers une plaque d'extrémité (23), la plaque d'extrémité étant en communication fluïdique avec la pluralité de canaux qui ont un intérieur creux et sont supportés par la plaque d'extrémité, et l'espace vide étant défini entre ladite pluralité de canaux ;
 - la filtration des particules de suie des gaz d'échappement en faisant circuler une partie des gaz au travers du treillis métallique éventuellement amovible dans l'intérieur creux du canal ;
 - l'écoulement d'une partie des gaz d'échappement au travers de l'espace vide, le vide ne comportant pas de treillis ; et
 - la diversion d'une grande partie des gaz d'échappement vers l'espace vide à mesure que l'accumulation des particules de suie dans le treillis métallique augmente.
15. Procédé selon la revendication 14, comprenant en outre la régulation de la quantité de gaz d'échappement s'écoulant au travers de l'espace vide en incorporant une ou plusieurs ouvertures d'orifice (34) dans la plaque d'extrémité.
16. Procédé selon la revendication 15, comprenant en outre l'abaissement de la température d'allumage des particules de suie filtrées dans les canaux par incorporation d'un catalyseur d'oxydation sur l'élément filtrant.

17. Procédé selon la revendication 16, comprenant en outre le brûlage des particules de suie filtrées dans les canaux.

18. Procédé selon la revendication 14, comprenant en outre l'oxydation de la partie des gaz d'échappement qui s'écoule au travers de l'espace vide en fournissant un catalyseur d'oxydation sur au moins une partie de l'extérieur des canaux.

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Fig. 1

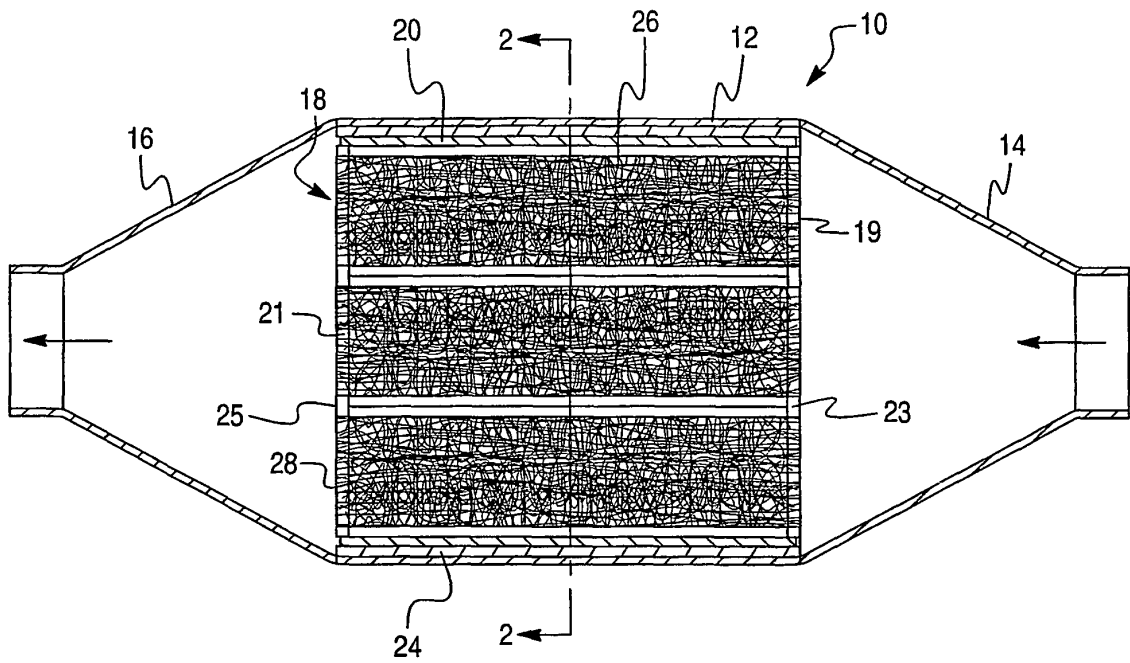


Fig. 2

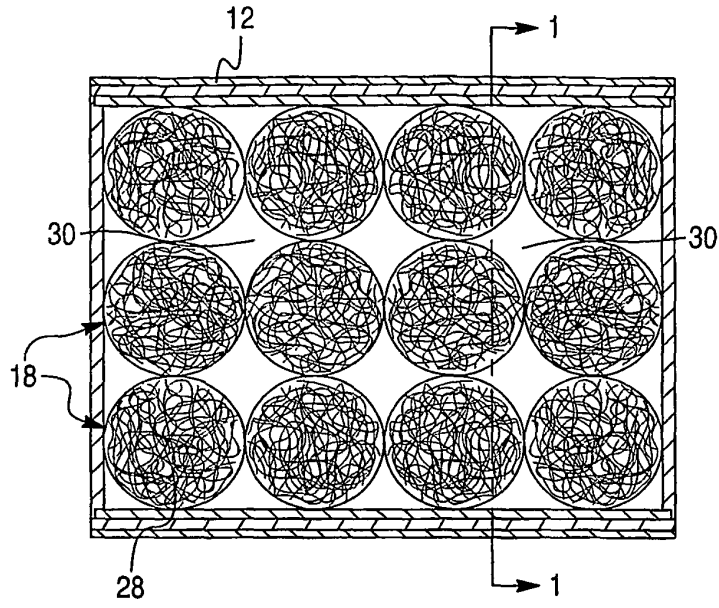


Fig. 3

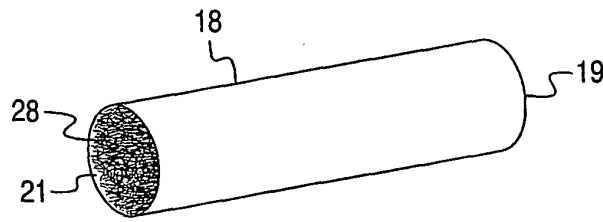
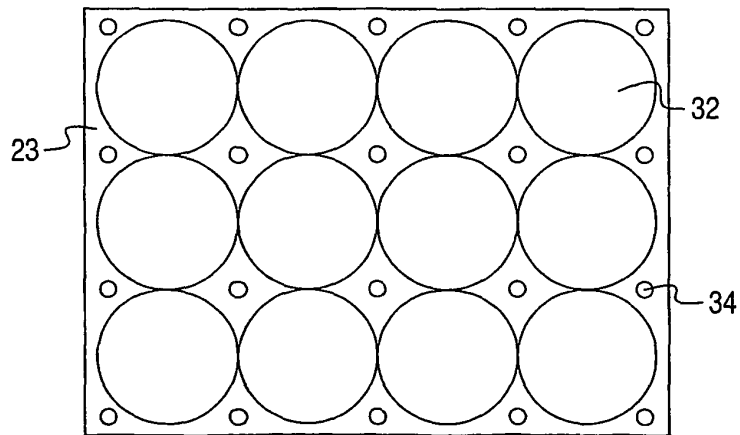


Fig. 4



REFERENCES CITED IN THE DESCRIPTION

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