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(54) **COMPOSITIONS FOR REDUCING ATMOSHERIC OXIDISING POLLUTANTS**

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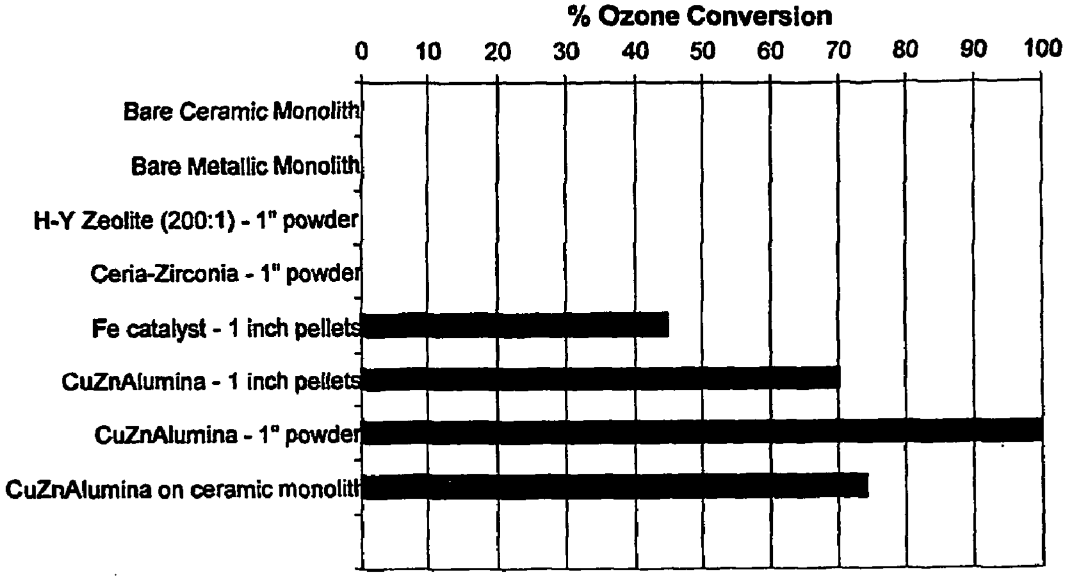
(57) **ABSTRACT**

A composition for reducing atmospheric oxidizing pollutants comprising a reducing agent comprising: at least one transition element and/or one or more compounds including at least one transition element wherein the standard electrode potential of the redox reaction including the transition element and an ionic species of the transition element or between the ionic species of the transition element present in the or each compound and a further ionic species of the transition element is less than +1.0 volt; a precious metal-free trap material capable of trapping at least one atmospheric reducing pollutant, whereby the at least one atmospheric oxidizing pollutant is reduced by a combination of the trap material and at least one trapped atmospheric reducing pollutant, which at least one trapped atmospheric reducing pollutant is consequently oxidized; or a manganese-based catalyst, preferably MnO_2 or a derivative thereof including cryptomelane, and a water soluble binder.



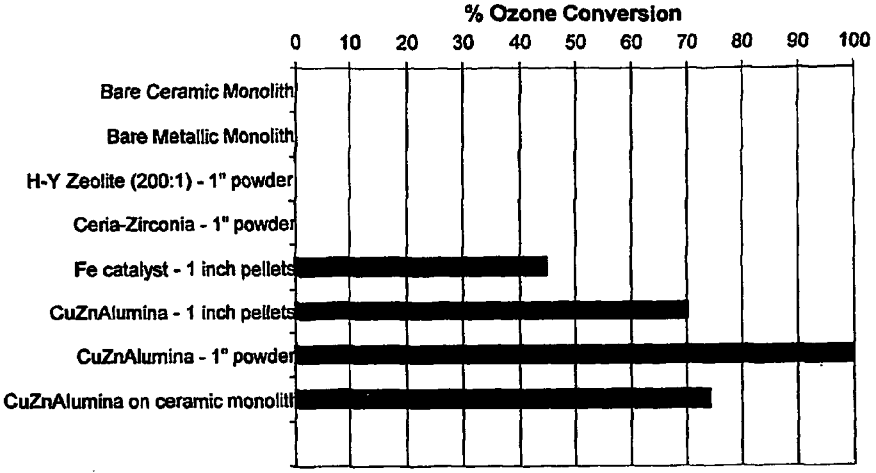

% Ozone Conversion
0
10
20
30
40
50
60
70
80
90
100
Bare Ceramic Monolith
Bare Metallic Monolith
H-Y Zeolite (200:1) - 1" powder
Ceria-Zirconia - 1" powder
Fe catalyst - 1 inch pellets
CuZnAlumina - 1 inch pellets
CuZnAlumina - 1" powder
CuZnAlumina on ceramic monolith

Fig. 1

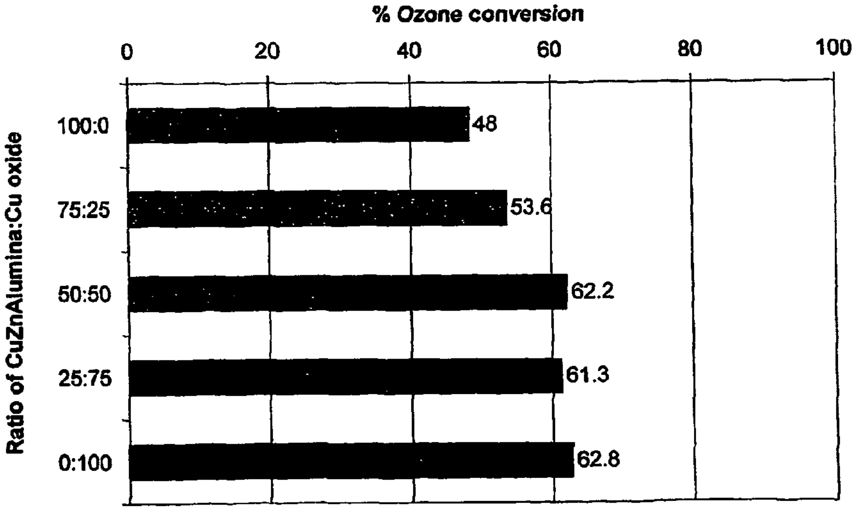

% Ozone conversion
0
20
40
60
80
100
Ratio of CuZnAlumina:Cu oxide
100:0
75:25
50:50
25:75
0:100
48
53.6
62.2
61.3
62.8

Fig. 2

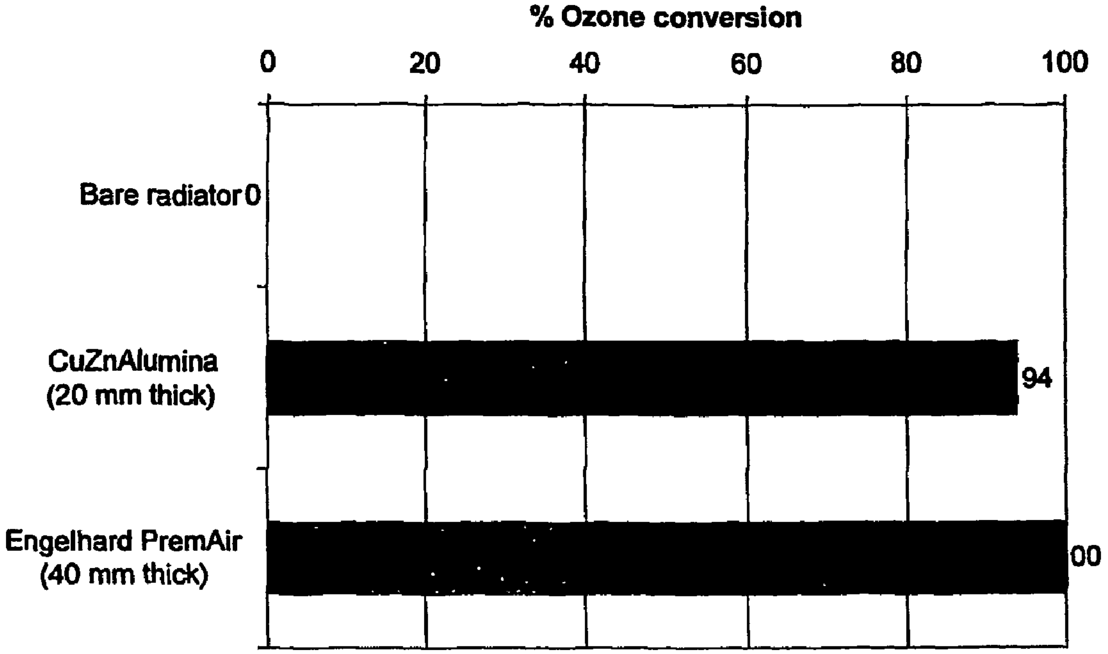

% Ozone conversion
0
20
40
60
80
100
Bare radiator
0
CuZnAlumina
(20 mm thick)
94
Engelhard PremAir
(40 mm thick)
00

Fig. 3

COMPOSITIONS FOR REDUCING ATMOSHERIC OXIDISING POLLUTANTS

[0001] The present invention relates to compositions for reducing atmospheric oxidising pollutants, such as ozone (O_3) and nitrogen dioxide (NO_2), and in particular to compositions for coating surfaces for contacting the atmosphere.

[0002] By "atmospheric oxidising pollutant" herein, we mean an atmospheric pollutant that has the potential to oxidise other atmospheric pollutants in a redox reaction. Examples of atmospheric oxidising pollutants include O_3, NO_2, dinitrogen tertroxide (N_2O_4) and sulfur trioxide (SO_3).

[0003] Ground-level O_3, a component of smog, is created from the reaction of nitrogen oxides (NOx) and hydrocarbons (HC), from vehicle and industrial emissions. Aldehydes, organic species having a relatively high Maximum Incremental Reactivity adjustment factor (MIR) also known as carter factors (as defined by "Californian Non-methane organic gases test procedures", The California Environmental Protection Agency Air Resource Board dated Aug. 5, 1999), are also produced. Part of this reaction is catalysed by sunlight and can be represented by two equations:

$$O_2+RCH_2CH_3+NO \rightarrow RCH_2CHO+NO_2\text{; and} \quad \text{(i)}$$

$$NO_2+O_2 \xrightarrow{hv} O_3+NO. \quad \text{(ii)}$$

[0004] Smog can cause asthma and respiratory ailments and is a particular problem in the southern California basin, Los Angeles and Houston, Tex. in the USA.

[0005] In WO 96/22146, Engelhard describes the concept of coating an atmosphere-contacting surface of a vehicle with a composition for treating one or more atmospheric pollutant, such as O_3 alone, O_3 and carbon monoxide (CO) or O_3, CO and HC. The surface is preferably that of a heat exchanger, such as a radiator or air conditioner condenser, located within the vehicle's engine compartment. As the vehicle is propelled through the atmosphere, pollutants suspended in the atmosphere contact the composition and, depending on the formulation of the composition, it catalyses the reduction of the atmospheric oxidising pollutant O_3 to oxygen, and/or the oxidation of the atmospheric reducing pollutant carbon monoxide to carbon dioxide and/or of HC to water and carbon dioxide.

[0006] Engelhard markets a vehicle radiator having a catalytic coating for reducing O_3 under the trade name PremAir®. Details of PremAir® can also be found on Engelhard's website at www.Engelhard.com/premair. It is also described in its WO 96/22146. We understand that the active material on the marketed radiators is a manganese-based component, cryptomelane ($KMn_8O_{16}.xH_2O$, structurally related to α-MnO_2). Coated radiators have been fitted on certain Volvo production passenger vehicles, e.g. the S80 luxury sedan in USA and throughout Europe.

[0007] Catalytically coated heat exchangers are also used for treating aeroplane cabin air and for reducing O_3 emissions from computer printers, photocopiers etc.

[0008] Modern heat exchangers for use in vehicles are made from aluminium or aluminium alloys and are manufactured by companies such as Visteon, Delphi and Valeo. Heat exchangers for non-vehicle applications can also be made from aluminium or aluminium alloys. Hereinafter "aluminium" will be used to refer to aluminium and alloys of aluminium.

[0009] Aluminium is a relatively reactive metal. For example, it is known that when aluminium is exposed to atmospheric oxygen it develops a surface coating of oxide. Accordingly, when an aluminium heat exchanger is coated with a catalytic coating, such as the cryptomelane-based composition used in Engelhard's Premair system, it is important that the composition does not react with the aluminium substrate. If the catalytic coating does react with and/or promote the corrosion of the aluminium substrate, this can drastically reduce the working life of the heat exchanger. In vehicle applications, heat exchangers are exposed to conditions which can promote metallic corrosion including moist air, salt and/or grit.

[0010] To test the ability of vehicle components to withstand corrosion, there have been devised certain standard laboratory cyclic salt spray corrosion tests termed "SWAAT" (e.g. ASTM G-85 A3 adapted from ASTM B117). Engelhard has been at pains to point out in its Society of Automotive Engineers (SAE) presentations (see SAE 982728 and 1999-01-3677) that the application of its catalytic coatings does not affect the resistance to corrosion of an aluminium radiator core and fully assembled radiators as tested by SWAAT. Furthermore, it has performed its own laboratory galvanic corrosion tests to show that brazed joints to the aluminium core are not prone to corrosion (see the SAE papers mentioned above). In the SWAAT test no leaks were detected following up to 1700 hours of the cyclic salt spraying of both Engelhard's coated aluminium radiator and a control un-coated aluminium radiator; independent tests concluded that, in the galvanic corrosion tests, no adverse galvanic corrosion effects would be expected from application of the reducing agent coating on aluminium radiators as shown by galvanic current measurements.

[0011] However, we believe that, in practice, the aluminium vehicle radiators including the PremAir® manganese-based catalytic coatings are indeed more susceptible to corrosion following prolonged use as compared with non-coated radiators. Without wishing to be bound by theory, we believe that this is because under acidic conditions, the oxidation potential of Mn^{4+} (the redox state of manganese in MnO_2) and Mn^{2+} as measured by the standard electrode potential is relatively high being +1.1406 volt. Increased corrosivity of a catalytic coating will have an economic impact on the vehicle manufacturer or its customer, in that the radiator will need to be replaced earlier than for an un-coated radiator, either within warranty or at the cost of the vehicle owner. Alternatively, or additionally, components of the composition including the catalytic material may contribute to the increased corrosion experienced in PremAir® coated radiators.

[0012] In our co-pending British patent application of the same filing date entitled "Agents for reducing atmospheric oxidising pollutants", the contents of which are incorporated herein by reference, we describe a number of alternative precious metal-free agents for reducing atmospheric oxidising pollutants such as O_3 to those described by Engelhard in WO 96/22146 that show similar or higher activity for O_3 reduction than Engelhard's manganese-based catalysts, e.g. cryptomelane, at the same ambient temperature. We believe that our alternative reducing agents are less likely to cause corrosion to an aluminium substrate in SWAAT and Engelhard's galvanic corrosion tests when compared with Engelhard's manganese-based compositions because the standard electrode potential of the redox reaction including the transition element and an ionic species of the transition element or between the ionic species of the transition element present in the or each compound and a further ionic species of the transition element is less than +1.0 volt.

[0013] In our co-pending British patent application of the same filing date entitled "Method of treating atmospheric pollutants", the contents of which are incorporated herein by reference, we describe how a precious-metal free trap material including at least one trapped atmospheric reducing pollutant, such as a hydrocarbon, can reduce at least one atmospheric oxidising pollutant Consequently, the at least one trapped atmospheric reducing pollutant itself is oxidised. One application for our observation is in treating atmospheric O_3 and hydrocarbons contacted by a vehicle by coating an atmosphere contacting surface such as a radiator with a composition including the trap material. Non-mobile applications are equally viable, as is explained in the above specification.

[0014] Modem radiators comprise a radiator core typically of aluminium, which core including fins or plates extending from the outer surface of a housing or conduit for carrying a fluid to be cooled. To this core is fitted one or more plastic tanks which carry the fluid to and from the radiator core. In the process for manufacturing PremAir® coated radiators, it is understood that the temperatures required to cure the catalyst composition applied to the radiator core are sufficient to heat damage plastic tanks. Accordingly, in the process used in practice, the coated radiator cores are prepared in a separate step before the plastic tanks are fitted thereto.

[0015] It would be a considerable advantage in the manufacture of coated heat exchangers to be able to cure the reducing agent composition at temperatures below which plastic components, such as plastic tanks for radiators, suffer heat damage. For example, this would avoid a number of steps of the manufacturing process used by Engelhard in making PremAir® coated radiators, thus saving energy in the curing process and making the process as a whole more time and cost efficient.

[0016] As will be appreciated by the person skilled in the art, the formulation of a composition suitable for application of a reducing agent to a surface is complex. In addition to the active reducing agent component, the formulation can include one or more binder (including thermosetting or thermoplastic polymeric binders), stabiliser, age resistor, dispersant, plasticiser, flow improver, water resistance agent or adhesion improvement agent. The binder provides cohesion to the composition. Furthermore, it provides adhesion of the "wet" composition to a substrate following application, and once cured, it provides adhesion and mechanical robustness to the coating to prevent it flaking after prolonged thermal cycling, and the ability to withstand knocks and bumps.

[0017] Among the factors that the skilled formulator will consider in formulating a composition including a reducing agent for coating, e.g. an aluminium alloy radiator, are the solvent medium and its compatibility with the other components and how the composition is to be used. For example, how does the composition handle, flow or mix? Will the composition separate or settle on standing? Does the formulation diminish the activity of the reducing agent, for example by preventing air accessing the component, by chemical reaction with the solvent or any other component in the formulation or does the curing process thermally deactivate the reducing agent? Is the composition suitable for the chosen mode of application, e.g. spray coating, electrostatic spray coating or screen-printing? Does the cured formulation have the required physical properties?

[0018] It can be seen, therefore, that the problem of developing a composition that cures at lower temperatures cannot be solved merely by exchanging the solvent of a known composition for one with a lower boiling point.

[0019] In WO 96/22146 Engelhard describe a number of polymeric binder components for use in the catalyst compositions described therein. The preferred polymers and copolymer binders are vinyl acrylic polymers and ethylene vinyl acetate copolymers. Cellulosic polymers are also mentioned but none of the Examples exemplify a composition including a cellulosic binder.

[0020] We have now found that, very surprisingly, water soluble binders are particularly suited to compositions for coating atmosphere contacting surfaces, which compositions include, as an active component, the precious metal-free reducing agents described in our co-pending British patent application of the same filing date entitled "Agents for reducing atmospheric oxidising pollutants", the trap materials per se described in our co-pending British patent application of the same filing date entitled "Method of treating atmospheric pollutants" or the catalysts described in WO 96/22146, particularly manganese-based catalysts such as MnO_2 and derivatives thereof, particularly cryptomelane. This observation provides a number of very useful advantages.

[0021] By "atmospheric reducing pollutant" herein, and as described in our co-pending British patent application of the same filing date entitled "Method of treating atmospheric pollutants", we mean an atmospheric pollutant that has the potential to reduce other atmospheric pollutants in a redox reaction. Non-limiting examples of atmospheric reducing pollutants are hydrocarbons including aliphatic hydrocarbons, e.g. alkanes, and cyclic hydrocarbons; paraffins; olefins, alkenes and alkynes; dialkenes including conjugated unsaturated hydrocarbons; carboxylic, peroxy or sulfonic acids; partially oxygenated hydrocarbons including aldehydes, conjugated aldehydes, ketones, ethers, alcohols and esters; amides; ammonium compounds; aromatic hydrocarbons and cycloparaffins; any of the above including one or more nitrogen-, sulfur-, oxygen- or phosphorus-atoms; CO; sulphur dioxide and soot or particulate matter components exhausted from, e.g. a power plant (as defined hereinbelow).

[0022] According to one aspect, the invention provides a composition for reducing atmospheric oxidising pollutants, which composition comprises a reducing agent comprising: at least one transition element and/or one or more compounds including at least one transition element wherein the standard electrode potential of the redox reaction including the transition element and an ionic species of the transition element or between the ionic species of the transition element present in the or each compound and a further ionic species of the transition element is less than +1.0 volt; a precious metal-free trap material capable of trapping at least one atmospheric reducing pollutant, whereby the at least one atmospheric oxidising pollutant is reduced by a combination of the trap material and at least one trapped atmospheric reducing pollutant, which at least one trapped atmospheric reducing pollutant is consequently oxidised; or a manganese-based catalyst, preferably MnO_2 or a derivative thereof including cryptomelane, and a water soluble binder.

[0023] Whilst the trap material per se embodiment of the present invention substantially does not decompose O_3, for the purposes of the present specification it is embraced within the meaning of “reducing agent”. See also our co-pending British patent application for further details.

[0024] An important advantage of the present invention is that the composition can be cured at relatively low temperatures, e.g. $\leqq 90°$ C., compared with compositions including Engelhard’s preferred binders. In particular, this feature enables the preparation of a radiator core fitted with its plastic tanks in a continuous process, i.e. without having first to prepare a coated core and then fit the plastic tanks thereto. In contrast with compositions requiring higher curing temperatures, the coated radiator core must be prepared before assembling the tanks to prevent heat damage of the tanks during curing. Thus, not only is there an economic advantage in that the energy required to cure the composition is reduced, but the process of radiator manufacture is simplified.

[0025] The composition according to the invention can be applied to a surface with known technology such as by spraying using a compressed air spray gun, by an electrostatic application process or using a screen printing process. Furthermore, the cured composition has acceptable physical properties as displayed by scrape, wipe, ultrasonic and SWAAT tests. In particular, no deterioration was seen following thermal cycling and the cured composition does not hydrate when contacted with aqueous media or flake or chip.

[0026] In one preferred embodiment, the water-soluble binder is a cellulosic binder. The cellulosic binder can be an ether or ester or semi-synthetic cellulosic binder, but is preferably hydroxypropyl- or methylellulose.

[0027] In another preferred embodiment, the water-soluble binder is a vinyl or acrylic binder, preferably polyvinyl alcohol or ammonium polymethacrylate.

[0028] Preferably, the transition element is copper, iron or zinc or a mixture of any two or more thereof. The or each compound including one or more transition element can be any suitable compound such as an oxide, carbonate, nitrate or hydroxide, but is preferably an oxide. In some circumstances, it is preferable to reduce the transition element in a transition element-including compound if in the reduced form the reducing agent is more active in its intended use. Compounds including transition elements prior to reduction can be referred to as ‘precursor’. For example, in a preferred embodiment the reducing agent is $CuO/ZnO/Al_2O_3$ is the precursor and the active form of the reducing agent is obtained by reducing the CuO to give $Cu/ZnO//Al_2O_3$. The reduced form of a transition element can be stabilised with suitable stabilisers as appropriate.

[0029] If supported, the transition element or transition element compound is preferably supported on a high surface area oxide selected from alumina, ceria, silica, titania, zirconia, a mixture or a mixed oxide of any two or more thereof.

[0030] According to preferred embodiments, the active form of the reducing agent is copper (II) oxide per se, a mixture of reduced copper (a) oxide and zinc oxide on an alumina support or iron oxide on a mixed alumina/ceria support.

[0031] Methods of manufacturing copper (II) oxide, copper (II) oxide and zinc oxide on Al_2O_3 or iron oxide on a mixed alumina/ceria support are known to a person skilled in the art or can be deduced by reasonable experimentation, e.g. by co-precipitation of the or each transition element component and/or support. For example, in a $CuO/ZnO//Al_2O_3$ reducing agent the Cu and Zn can be co-precipitated and the already formed Al_2O_3 added thereto. Specific details of the manufacturing processes will not be given here.

[0032] The $CuO/ZnO//Al_2O_3$ reducing agent composition can be any suitable for the intended e.g. $CuO30:ZnO60:Al_2O_3$ 10 or $CuO60:ZnO30:Al_2O_3$ 10. Commercially available forms of these compositions are available from ICI as ICI 52-1 and ICI 51-2 respectively. Commercially available $CuO/ZnO//Al_2O_3$ is sold as pellets, which can be ground to the required particle size.

[0033] Preferred precious metal-free trap materials include high surface area inorganic species such as zeolites, other molecular sieves, crystalline silicates, crystalline silicate-containing species, aluminas, silicas, (optionally amorphous) aluminosilicates, layered clays and aluminium phosphates. Where the trap material is zeolite, we prefer beta-zeolite or zeolite Y and most preferably ZSM-5, optionally metal-substituted, so long as the metal substituted zeolite does not decompose O_3 per se, e.g. the zeolite is not transition metal substituted.

[0034] According to a further aspect, the invention provides a method of making an atmosphere-contacting surface according to the invention comprising the steps of coating the surface with the composition and heating the coated surface to $\leqq 90°$ C. for a sufficient time to cure the composition.

[0035] In a preferred embodiment, the atmosphere-contacting surface is associated with a means for causing movement of the surface relative to the atmosphere.

[0036] In a preferred embodiment the means for causing movement of the surface relative to the atmosphere is a power plant. The power plant can be an engine fuelled by gasoline, diesel, liquid petroleum gas, natural gas, methanol, ethanol, methane or a mixture of any two or more thereof, an electric cell, a solar cell or a hydrocarbon or hydrogen-powered fuel cell.

[0037] Preferably the atmosphere-contacting surface is on or in a vehicle, and the movement-causing means is a power plant as described above. The vehicle can be a car, van, truck, bus, lorry, aeroplane, boat, ship, airship or train, for example. A particularly preferred application is for use in heavy-duty diesel vehicles, i.e. vans, trucks, buses or lorries, as defined by the relevant European legislation.

[0038] The atmosphere-contacting surface can be any suitable surface that encounters and contacts the atmosphere, most preferably, at relatively large flow rates as the vehicle moves through the atmosphere. The support surface is preferably located at or towards the front end of the vehicle so that air will contact the surface as the vehicle is propelled through it. Suitable support locations are fan blades, wind deflectors, wing mirror backs or radiator grills and the like. Alternative locations for supporting the reducing agent are given in WO 96/22146 and are incorporated herein by reference.

[0039] In a most preferred embodiment the apparatus comprises a heat exchange device such as a radiator, an air conditioner condenser, an air charge cooler (intercooler or aftercooler), an engine oil cooler, a transmission oil cooler or a power steering oil cooler. This feature has the advantage that the heat exchange device reaches above ambient temperatures, such as up to 140° C., e.g. 40° C. to 110° C., at which, for example, O_3 reduction can occur more favourably. A further advantage of using heat exchangers as the support surface for the or each reducing agent composition is that in order to transfer heat efficiently they have a relatively large surface area comprising fins or plates extending from the outer surface of a housing or conduit for carrying a fluid to be cooled. A higher surface area support surface provides for a greater level of contact between the each reducing agent composition and the atmosphere.

[0040] By "ambient" herein we mean the temperature and conditions, e.g. humidity, of the atmosphere.

[0041] In a particularly preferred embodiment, the apparatus comprises a radiator and/or air conditioning condenser which is housed within a compartment of a vehicle also including the power plant, e.g. an air-cooled engine. This provides the advantage that the radiator and/or condenser is exposed to ambient atmospheric air as the vehicle is propelled through the atmosphere whilst being protected by the radiator grill from damage by particulates, e.g. grit or stones, and from the impact of flies. For mid- and rear-engine vehicles, air intakes and conduits can be arranged to carry atmospheric air to and from the supported reducing agent. A further advantage of locating the radiator and/or condenser in the engine compartment is that exposure to corrosion-causing agents such as moist air, salt and/or grit is reduced and hence so too is the rate of any corrosion. Whilst the radiator and/or condenser can be formed of any material, it is usually a metal or an alloy. Most preferably, the heat exchanger is aluminium or an alloy containing aluminium.

[0042] Where the atmosphere-contacting surface is of a heat exchanger, it is important that the composition coating the surface does not reduce the effectiveness of the substrate to transfer heat. Accordingly, in one preferred feature, the composition of the invention can include particles of a transition metal, preferably silver or copper, for improving the thermal conductivity of the composition.

[0043] Another advantage of using a heat exchanger, such as a radiator, as the support surface for the reducing agent is that the radiator is releasably attached to a vehicle, typically in the engine compartment of the vehicle. This enables coated radiators and other heat exchangers to be retrofitted to the vehicle, e.g. during normal servicing of the vehicle, thereby to improve the pollutant treating ability of the vehicle.

[0044] Alternatively the apparatus can be non-mobile, and the surface is associated with the movement-causing means to provide the required relative movement between the surface and the atmosphere. For example, the surface can be one or more blades for causing movement of air. In one embodiment the blades are fan blades for cooling a stationary power plant such as for powering an air conditioning unit or advertising hoarding. In another embodiment the blade is a fan or turbine blade for drawing air into the air conditioning system of a building.

[0045] In addition to, or instead of, the support surface being on a fan or turbine blade, the surface can be the internal surfaces of pipes, tubes or other conduits for carrying atmospheric air, e.g. in an air conditioning system for a vehicle or a building and condenser elements in air conditioning units provided that the movement of the air is caused by a movement causing means.

[0046] That the reducing agents for use in the present invention are at least as active for reducing O_3 as Engelhard's Premair® manganese-based components is shown in Example 4 below, where a 20 mm thick aluminium radiator coated with a composition including our mixture of "reduced" copper (II) oxide and zinc oxide on an alumina support gave a % O_3 conversion of 94% whereas the commercially available 40 mm thick Premair® aluminium radiator including cryptomelane had a % O_3 conversion of 100%. From Example 1 we know that O_3 conversion activity improves significantly if the reducing agent loading is doubled. Therefore, if our coating were applied on a 40 mm thick unit at the same mass per unit volume, we would expect the O_3 conversion to improve from 94%, probably to 100%.

[0047] In order that the invention may be more fully understood, the invention will now be described by reference to the following illustrative Examples and by reference to the accompanying drawings, in which:

[0048] **FIG. 1** is a bar chart showing the % O_3 conversion for various candidate reducing agents;

[0049] **FIG. 2** is a bar chart showing the effect on % O_3 conversion of increasing CuO content on the O_3 conversion of $CuO/ZnO//Al_2O_3$; and

[0050] **FIG. 3** is a bar chart comparing the % O_3 conversion of a composition including a mixture of copper (II) oxide and zinc oxide on an alumina support and a hydroxypropyl cellulose binder with a bare radiator and a Premair® radiator.

EXAMPLE 1

[0051] To screen candidate O_3 reducing agents at room temperature, a test rig comprising an upstream O_3 generator, a stainless steel tube including metal mesh to pack a reactor bed material therebetween and a downstream O_3 detector was set up in a fume cupboard. O_3 was generated and mixed with air before passing through the reactor bed containing powder or pellet samples. The exhaust gas from the reactor bed was passed through the O_3 detector (measured in 5 ppm units) before being vented. An inlet O_3 concentration of 200 ppm at a space velocity (GHSV) of ~1000/hr was used. Whilst higher space velocities would be observed at, e.g. the surface of a radiator, and atmospheric O_3 concentrations are present in the parts per billion range, the results were useful to compare directly the potential of each material tested to reduce O_3.

[0052] The following materials were tested: H—Y zeolite (Si:Al ratio 200:1)—1" powder bed; a ceria-zirconia mixed oxide 1" powder (ceria-zirconia mixed oxide is an oxygen storage component used in three way catalyst compositions); iron oxide on a ceria support (hereinafter "Fe reducing agent")—1" pellet bed; Cu/ZnO//Al_2O_3—1" pellet bed; Cu/ZnO//Al_2O_3—1" powder bed; and Cu/ZnO//Al_2O_3 on a ceramic monolith.

[0053] **FIG. 1** shows the results of a comparison of the O_3 decomposition activity of these materials tested in the rig described above at room temperature. No O_3 conversion was observed for the empty system or over a bare metallic or ceramic substrate. Zeolite and ceria-zirconia were also found to have no O_3 decomposition activity. The best material tested was Cu/ZnO//Al_2O_3; this gave approximately 70% conversion over a 1" bed of pellets, compared to 45% for a 1" bed of Fe reducing agent. Cu/ZnO//Al_2O_3 coated onto a ceramic monolith. As expected, the form of the reducing agent material was important—after grinding the Cu/ZnO//Al_2O_3 pellets into a fine powder, the O_3 conversion increased to 100%.

[0054] It was also confirmed that the O_3 conversion is dependent on the reducing agent loading. For Cu/ZnO//Al_2O_3 powder, as the loading increased from 0.5 to 1 g the O_3 conversion increased from 48 to 63%. At higher loadings 100% conversion was achieved. A similar trend was observed for the Fe reducing agent; doubling the reactor bed depth from 1" to 2" increased the O_3 conversion from 45 to 100%, while reducing the bed depth to ½" reduced the O_3 conversion to 25%.

EXAMPLE 2

[0055] To test whether the O_3 conversion of our best candidate O_3 reducing agent Cu/ZnO//Al_2O_3 can be improved by including copper (II) oxide, a series of materials were prepared by mixing Cu/ZnO//Al_2O_3 and copper (II) oxide at ratios of 100:0, 75:25, 50:50, 25:75 and 0:100 by mass. The O_3 conversion was measured using the rig and procedure described in Example 1 above for 0.5 g of each powder and the results are shown in **FIG. 2**. They clearly show that adding copper oxide increases the O_3 conversion from 48% for the undoped material to ~62% for material with $\geqq$50% copper oxide.

EXAMPLE 3

[0056] There is now described a composition including the Cu/ZnO//Al_2O_3 reducing agent component for application to e.g. an aluminium alloy radiator substrate.

[0057] Cu/ZnO//Al_2O_3 was mixed with an aqueous solution of hydroxypropyl cellulose binder, Klucel™, to a concentration of 10% wt/wt. The coating was applied to each side of a Visteon aluminium alloy radiator of 20 mm thickness using a compressed air spray gun and then cured at or below 90° C.

EXAMPLE 4

[0058] There is now described a composition including a beta zeolite trap component for application to an aluminium radiator substrate. Beta zeolite was mixed with an aqueous solution of hydroxypropyl cellulose binder, Klucel™, to a concentration of 10% wt/wt. The coating was applied to each side of a Visteon aluminium radiator of 20 mm thickness using a compressed air spray gun and then cured at up to 90° C.

EXAMPLE 5

[0059] This Example is designed to compare the O_3 conversion activity of our Cu/ZnO//Al_2O_3 reducing agent with that of Engelhard's Premair® catalyst.

[0060] A Ford Mondeo radiator manufactured by Visteon was supplied for coating. This radiator, consisting of uncoated aluminium foil, has a face area of 16"×10" and a thickness of 20 mm. The unit was coated with a washcoat including the Cu/ZnO//Al_2O_3 and a 10% wt/wt aqueous solution of a hydroxypropyl cellulose binder (trade name "Klucel") described in Example 3 above using a compressed air spray gun. Two layers were applied to each side, loading of 68 g or 0.54 g/in^3. After drying, the radiator was found to have a thick, dark brown coating of approximately 20 mm total thickness which had acceptable adhesion and resisted most physical abrasion.

[0061] The activity of the coated radiator was tested and compared to a bare aluminium alloy radiator and an Engelhard Premair coated aluminium alloy radiator. Activity testing was carried out in a similar manner to the material screening described in Example 1 above, with the powder bed reactor modified so that it clamped onto either side of the radiator. The results can be seen in **FIG. 3**. 94% O_3 conversion was obtained over the Cu/ZnO//Al_2O_3 coated aluminium radiator; this compared favourably with the 100% conversion obtained over the Premair® radiator. The thickness of the Premair® radiator was approximately 40 mm, twice that of the radiator coated with our Cu/ZnO//Al_2O_3 composition. No conversion was obtained from a bare radiator.

1. A heat exchanger comprising an atmosphere-contacting surface coated with a composition for reducing atmospheric oxidising pollutants, which composition comprises a reducing agent comprising a manganese-based catalyst and a water soluble binder.

2. A heat exchanger according to claim 1, wherein the manganese-based catalyst is MnO_2 or a derivative thereof.

3. A heat exchanger according to claim 2, wherein the MnO_2 derivative is cryptomelane.

4. A heat exchanger according to claim 1, wherein the water-soluble binder is a cellulosic binder.

5. A heat exchanger according to claim 4, wherein the cellulosic binder is selected from the group consisting of an ether ester and semi-synthetic cellulosic binder.

6. A heat exchanger according to claim 1, wherein the water soluble binder is a vinyl or acrylic binder.

7. A heat exchanger according to claim 1, wherein the manganese-based catalyst is supported on a high surface area oxide selected from the group consisting of alumina, ceria, silica, titania, zirconia and a mixed oxide of any two or more thereof.

8. A heat exchanger according to claim 1, wherein the composition further comprises particles of a transition metal for improving the thermal conductivity of the composition.

9. A heat exchanger according to claim 1, wherein the surface comprises aluminium or an aluminium alloy.

10. A heat exchanger according to claim 1, wherein the heat exchanger is a radiator and/or a condenser.

11. A method of making a heat exchanger comprising an atmosphere-contacting surface coated with a composition for reducing atmospheric oxidising pollutants, which composition comprises a reducing agent comprising a manganese-based catalyst and a water soluble binder, which method comprises the steps of coating the surface with the composition and heating the coated surface for a sufficient time to cure the composition, wherein the heating step consists of heating the coated surface to ≦90° C.

12. A heat exchanger according to claim 4, wherein the cellulosic binder is hydroxypropyl- or methylcellulose.

13. A heat exchanger according to claim 1, wherein the water soluble binder is polyvinyl alcohol or ammonium polymethacrylate.

14. A heat exchanger according to claim 8, wherein the transition metal is silver or copper.

15. A heat exchanger according to claim 10, wherein the radiator and/or a condenser is part of a motor vehicle.

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