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

(11) EP 0 950 854 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.10.1999 Bulletin 1999/42

(51) Int Cl.6: **F23D 14/72**, F23Q 9/00

(21) Application number: **99302774.7**

(22) Date of filing: **09.04.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **10.04.1998 JP 9897698**
29.03.1999 JP 8539799

(71) Applicant: **Rinnai Kabushiki Kaisha**
Nagoya-shi, Aichi-ken (JP)

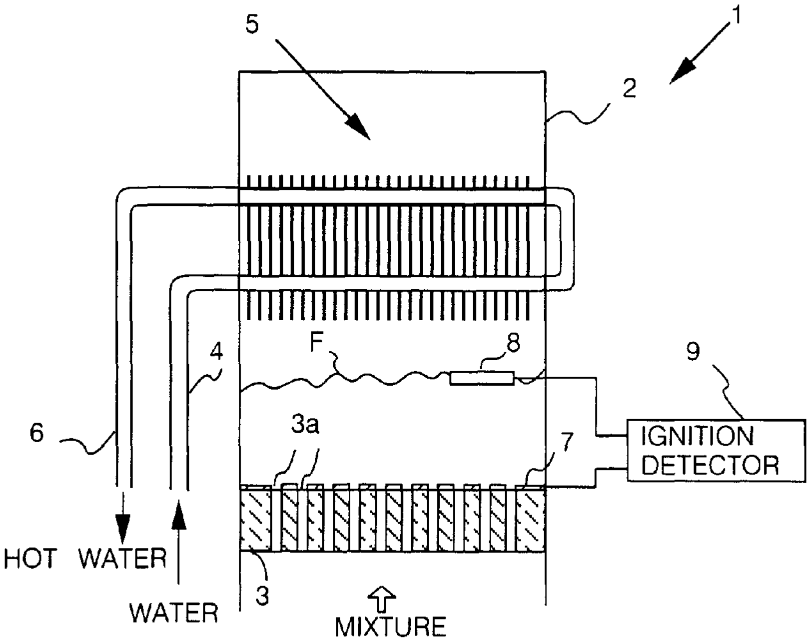
(72) Inventors:
- **Sobue, Tsutomu, c/o Rinnai Kabushiki Kaisha Nagoya-shi, Aichi-ken (JP)**
- **Ohashi, Ryusei, c/o Rinnai Kabushiki Kaisha Nagoya-shi, Aichi-ken (JP)**

(74) Representative: **Abrams, Michael John et al**
Haseltine Lake & Co.,
Imperial House,
15-19 Kingsway
London WC2B 6UD (GB)

(54) Combustion device

(57) A combustion device has a ceramic burner (3) comprising a porous ceramic plate having a plurality of burner ports (32) defined therein, an electrically conductive layer (7) disposed on a surface of the ceramic burner where flames are produced, an electric conductor (8) disposed in facing relation to the electrically conductive layer, and an ignition detector (9) for detecting a flame current flowing through the flames (F) to detect an ignition when a voltage is applied between the electrically conductive layer and the electric conductor. The electrically conductive layer is made of an electrically conductive perovskite-type metal oxide.

FIG.1



Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

Field of the Invention:

[0001] The present invention relates to a combustion device having a ceramic burner.

Description of the Related Art:

[0002] There has heretofore been known a combustion device having a burner which is supplied with a mixture of a fuel gas and air added at a predetermined ratio and burns the supplied mixture in total primary combustion. The burner comprises a ceramic burner having a ceramic plate which is porous to make itself resistant to thermal shocks. The ceramic plate has a number of small-diameter burner ports defined therein and extending from a surface of the plate to the opposite surface thereof.

[0003] In combustion devices, it has been general practice to apply a voltage is between a burner and a frame rod and detect a flame current flowing through flames produced by the burner for detecting an ignition. If a flame current in excess of a predetermined level is detected, then it is confirmed that the mixture has well been ignited. If the flame current falls below the predetermined level while the mixture is being combusted by the burner, then the burner is determined as suffering a flame failure. Since the ceramic burner is electrically nonconductive and no current flows therethrough, however, it is difficult to detect an ignition on the ceramic burner based on the flame current.

[0004] In view of the above drawback, it has been proposed to construct a ceramic burner of an electrically conductive ceramic material. One example of electrically conductive ceramic material is lithia-based ceramics such as petalite ($LiAlSi_4O_{10}$), for example.

[0005] A study by the inventors of a ceramic burner of petalite has revealed that when a voltage is applied between the ceramic burner of petalite and the flame rod, a produced flame current largely varies depending on the surface temperature of the ceramic burner. Specifically, the flame current that flows between the ceramic burner of petalite and the flame rod is as small as if the burner were made of an electrically nonconductive material when the surface temperature of the ceramic burner is low, and therefore it takes a considerable period of time until the flame current reaches a level high enough to be detected. The ceramic burner of petalite is further disadvantageous in that when burning conditions are changed while the mixture is being combusted or the mixture is re-ignited after the combustion of the mixture has been stopped, the flame current suffers a large overshoot, and will be stabilized after a long period of time. If the overshoot of the flame current is large, then the flame current tends to be too large to detect an ignition or a flame failure, and hence an ignition or a flame failure cannot be detected until the flame current becomes stabilized.

[0006] Japanese laid-open utility model publication No. 1-67466 and Japanese utility model publication No. 5-18606 disclose combustion devices in which an electrically conductive layer is placed on a surface of a ceramic burner where flames are produced. According to the disclosed combustion devices, a flame rod is disposed in confronting relation to the electrically conductive layer where flames are produced by the ceramic burner, and a voltage is applied between the electrically conductive layer and the flame rod. Alternatively, a voltage is applied between the electrically conductive layer and a heat exchanger which is employed in place of the flame rod. The publications referred to above state that the disclosed arrangement allows a flame current flowing through the flames to be detected to detect an ignition.

[0007] It is known that a deposited film of nickel is disposed as the electrically conductive layer on the surface of the ceramic burner. However, the deposited film of nickel cannot withstand use over a long period of time because nickel is poor in heat resistance.

[0008] If a deposited film of platinum or palladium which is highly resistant to heat is used instead of the deposited film of nickel, then it can be of stable service for a long period of time. Using such a deposited film of platinum or palladium inevitably results in an increase in the cost of the combustion device because these materials are precious metals and expensive.

[0009] Another solution is to use a deposited film of silicon carbide (SiC) instead of the deposited film of nickel. Silicon carbide is highly heat-resistant in air and can be utilized as an electrically conductive material as it is an intrinsic semiconductor. Therefore, silicon carbide is suitable for use as an electrically conductive material deposited on a ceramic burner surface. A deposited film of silicon carbide can be produced when silicon dioxide and carbon or silicon and carbon react with each other and then the reaction product is baked.

[0010] If a film of silicon carbide is to be deposited on a porous ceramic plate of a ceramic burner, however, since a high-temperature heat-treatment process is necessary to produce the deposited film of silicon carbide, the porous ceramic plate is rendered dense, and its resistance to thermal shocks is lowered. If the above reaction product is baked at a temperature which is not sufficiently high to make the porous ceramic plate dense, then it is difficult to produce a deposited film of silicon carbide.

[0011] The process of baking silicon carbide requires an additive of boron, carbon, or the like. However, a deposited film of silicon carbide produced with an added impurity tends to suffer reduced strength at high temperatures. Therefore, it is not easy to establish proper baking conditions. Furthermore, inasmuch as silicon carbide deteriorates if oxidized while being baked, the baking facility needs to be evacuated to prevent silicon carbide from being oxidized. Accordingly, the baking facility is complex and large in scale, tending to increase the cost of the combustion devices.

SUMMARY OF THE INVENTION

[0012] It is therefore an object of the present invention to provide a combustion device which includes a ceramic burner having an electrically conductive layer that is highly resistant to heat, relatively inexpensive, and can easily be manufactured.

[0013] To achieve the above object, there is provided in accordance with the present invention a combustion device comprising a ceramic burner comprising a porous ceramic plate having a plurality of burner ports defined therein, an electrically conductive layer disposed on a surface of the ceramic burner where flames are produced, an electric conductor disposed in facing relation to the electrically conductive layer, and ignition detecting means for detecting a flame current flowing through the flames to detect an ignition when a voltage is applied between the electrically conductive layer and the electric conductor, the electrically conductive layer being made of an electrically conductive perovskite-type metal oxide.

[0014] The ceramic plate of the ceramic burner can be manufactured inexpensively as a thermal-shock-resistant ceramic plate which is made of porous ceramics produced by baking particles of a fire-resistant, low-expansion ceramic material. The fire-resistant, low-expansion ceramic material may be cordierite, spodumene, aluminum titanate, mullite, zirconia, zircon, magnesia (including spinel and forsterite), alumina (including corundum), calcia, chromium oxide, dolomite, sillimanite, silica stone, zircon mullite, a mixture of alumina and zirconia, a mixture of alumina and zircon, or a mixture of two or more of the above materials, or the like.

[0015] The ceramic burner may be constructed of a dense ceramic plate. The dense ceramic plate may be manufactured by baking particles of a low-expansion ceramic material such as petalite, spodumene, eucryptite, aluminum titanate, zirconium potassium phosphate, or the like. However, the baking temperature is relatively high and a certain amount of energy is required to achieve the relatively high baking temperature. The electrically conductive layer may be formed on the dense ceramic plate by vacuum evaporation, CVD, or the like. However, it is necessary to roughen the surface of the dense ceramic plate for the purpose of increasing the bonding strength between the ceramic plate and the electrically conductive layer.

[0016] Consequently, if the dense ceramic plate is used, the cost of manufacture of the dense ceramic plate and the cost of manufacture of the electrically conductive layer. According to the present invention, the porous ceramic plate is used for reducing the cost of manufacture of the ceramic burner.

[0017] The perovskite-type metal oxide is represented by a general formula ABO_3 where A and B represent metals and O represents oxygen. Some perovskite-type metal oxides exhibit metallic electric conductor properties or semiconductor properties. According to the present invention, the electrically conductive layer is formed of a perovskite-type metal oxide which exhibits metallic electric conductor properties or semiconductor properties. The perovskite-type metal oxide may be represented by the above general formula where the metal A or a portion of the metals A, B is replaced with another metal.

[0018] The electrically conductive layer is produced by coating the ceramic plate with an aqueous slurry comprising a powder of electrically conductive perovskite-type metal oxide mixed with a solvent such as water or the like, drying the slurry, and baking the dried slurry. Since the perovskite-type metal oxide itself is inexpensive and does not require any special device for avoiding its oxidization because it is already an oxide. Therefore, the cost of manufacture of the combustion device is relatively low. The perovskite-type metal oxide is highly resistant to heat as it is already an oxide.

[0019] Preferably, the electrically conductive layer uniformly covers the surface of the porous ceramic plate, and the electrically conductive perovskite-type metal oxide enters surface pores in the ceramic plate.

[0020] The electrically conductive layer can exhibit uniform electric conductivity by uniformly coating the surface of the ceramic plate therewith. When the perovskite-type metal oxide is baked as described above, the perovskite-type metal oxide and the ceramic plate jointly make up a solid solution at their contacting surfaces. Therefore, the electrically conductive layer and the ceramic plate are firmly bonded to each other. Since the perovskite-type metal oxide entering the surface pores and the ceramic plate jointly make up the solid solution as described above, the electrically conductive layer is securely anchored to the ceramic plate.

[0021] The electrically conductive layer should preferably comprise particles of the electrically conductive perovskite-type metal oxide which have diameters ranging from 0.04 to 5 μm. The diameters referred to herein are those of the particles of the electrically conductive perovskite-type metal oxide after it has been baked.

[0022] If the particle diameters of the baked electrically conductive perovskite-type metal oxide were less than 0.04 μm, then it would be difficult for the electrically conductive layer to uniformly cover the surface of the ceramic plate. If the particle diameters of the baked electrically conductive perovskite-type metal oxide were greater than 5 μm, the solid solution would be difficult to form, and the electrically conductive layer would easily be peeled off the ceramic burner.

[0023] In order to uniformly cover the surface of the ceramic plate, the electrically conductive layer should preferably have a thickness ranging from 10 to 300 μm. If the thickness of the electrically conductive layer were smaller than 10 µm, then the ceramic plate would be liable to be exposed and the electrically conductive layer would not exhibit uniform electric conductivity. If the thickness of the electrically conductive layer exceeded 300 µm, then the electrically conductive layer would tend to crack due to thermal expansion upon baking, and would easily be peeled off the ceramic burner.

[0024] Preferably, the electrically conductive layer contains an inorganic binder ranging from 1 to 20 weight % of the total amount thereof, and the electrically conductive layer is bonded to the porous ceramic plate by the inorganic binder. Since the electrically conductive layer contains the inorganic binder, particles of the perovskite-type metal oxide are firmly bonded to each other or to the ceramic plate by the inorganic binder. The electrically conductive layer which contains the inorganic binder is effective to lower a baking temperature at which to bake the perovskite-type metal oxide and increase the range of baking temperatures at which the baked perovskite-type metal oxide acts as the electrically conductive layer. Therefore, it is made easy to establish a desired baking temperature.

[0025] The inorganic binder may be borosilicate glass, soda lime glass, etc. If the content of the inorganic binder were less than 1 weight % of the total weight of the electrically conductive layer, then the inorganic binder would fail to act as a binder. If the content of the inorganic binder were greater than 20 weight % of the total weight of the electrically conductive layer, then the resistance of the electrically conductive layer would be too large.

[0026] The electrically conductive perovskite-type metal oxide should preferably comprise $La_{1-x}Sr_xMnO_3$ because it exhibits electric conductivity and can easily be manufactured.

[0027] Furthermore, since $La_{1-x}Sr_xMnO_3$ has a high emissivity, the electrically conductive layer on the surface of the ceramic burner is effective to lower the temperature of flames, thus reducing nitrogen oxides emitted upon combustion by the ceramic burner. Moreover, because $La_{1-x}Sr_xMnO_3$ has a catalytic action for fully oxidizing methane contained in a town gas at low temperatures, it is capable of further reducing nitrogen oxides emitted upon combustion by the ceramic burner.

[0028] The above and other objects, features, and advantages of the present invention will become apparent from the following description when taken in conjunction with the accompanying drawings which illustrate preferred embodiments of the present invention by way of example.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029]

FIG. 1 is a schematic cross-sectional view of a combustion device according to the present invention;

FIG. 2 is a graph showing flame currents detected between an electrically conductive layer and a flame rod in response to input powers in a predetermined range in the combustion device according to the present invention;

FIG. 3 is a graph showing temperature-dependent changes in the electric conductivity of an electrically conductive perovskite-type metal oxide in the combustion device according to the present invention;

FIG. 4 is a graph showing changes in flame currents in response to input powers in a ceramic burner of the combustion device according to the present invention and other ceramic burners;

FIG. 5(a) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time an excess air ratio is 1.4 and the combustion device is set to a maximum combustion capability;

FIG. 5(b) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time an excess air ratio is 1.4 and the combustion device is set to a minimum combustion capability;

FIG. 6(a) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time an excess air ratio is 1.1 and the combustion device is set to a maximum combustion capability;

FIG. 6(b) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time an excess air ratio is 1.1 and the combustion device is set to a minimum combustion capability;

FIG. 7(a) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time burning conditions are changed during combustion;

FIG. 7(b) is a graph showing time-dependent changes in flame currents in the ceramic burner of the combustion device according to the present invention and the other ceramic burners at the time the mixture is extinguished after combustion and then re-ignited; and

FIG. 8 is a graph showing the relationship between contents of an inorganic binder in an electrically conductive layer, baking temperatures, and electric resistances of the electrically conductive layer in the combustion device according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0030] FIG. 1 shows a combustion device 1 according to the present invention which comprises a ceramic burner 3 housed in a casing 2 and a heat exchanger 5 also housed in the casing 2 for heating water supplied from a water supply pipe 4 with the ceramic burner 3 thereby to produce hot water. The combustion device 1 has a hot water supply pipe 6 for supplying hot water produced by the heat exchanger 5 to various places including a kitchen, a washroom, a bathroom, etc.

[0031] The ceramic burner 3 has a thermal-shock-resistant ceramic plate made of porous ceramics produced by baking particles of cordierite which is a fire-resistant, low-expansion ceramic material. The ceramic plate has a number of small-diameter burner ports 3a defined therein and extending from a surface of the plate to the opposite surface thereof. The ceramic burner 3 has an electrically conductive layer 7 disposed on a surface thereof facing the heat exchanger 5, the electrically conductive layer 7 comprising a coated layer of an electrically conductive perovskite-type metal oxide.

[0032] The combustion device 1 also has a frame rod 8 disposed between the ceramic burner 3 and the heat exchanger 5, and an ignition detector 9 for detecting an ignition by the ceramic burner 3. The ignition detector 9 detects an ignition by detecting a flame current that flows through flames F when a voltage is applied between the electrically conductive layer 7 and the flame rod 8 to ignite a mixture of a fuel gas and air supplied to the ceramic burner 3.

[0033] The porous ceramic plate which is produced by baking particles of cordierite has surface pores each having a size ranging from 3 to 200 μm. The porous ceramic plate with such surface pores has a good level of resistance to thermal shocks.

[0034] Electrically conductive perovskite-type metal oxides which exhibit metallic electric conductor properties include, for example, $SrTiO_3$, $BaTiO_3$, $LaTiO_3$, $CaVO_3$, $SrVO_3$, $CaCrO_3$, $SrCrO_3$, $CaFeO_3$, $SrFeO_3$, $SrCoO_3$, $LaNiO_3$, etc. Electrically conductive perovskite-type metal oxides which exhibit semiconductor properties include, for example, $CaTiO_3$, $BaVO_3$, $LaCrO_3$, $CaMnO_3$, $LaMnO_3$, $BaFeO_3$, $LaFeO_3$, $BaCoO_3$, $SrNiO_3$, $BaNiO_3$, $LnCrO_3$ (Ln = Pr, Nd, Sm, Eu), etc. Electrically conductive perovskite-type metal oxides which exhibit metallic electric conductor properties and semiconductor properties include, for example, $LaCoO_3$, etc.

[0035] The electrically conductive perovskite-type metal oxides may exhibit metallic electric conductor properties or semiconductor properties by replacing a portion of the metal A or B with another metal in the above general formula. Such electrically conductive perovskite-type metal oxides include, for example, $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$, $La_{1-x}Sr_xCoO_3$, $La_{1-x}Sr_xCrO_3$, $La_{1-x}Ca_xCrO_3$, $La_{1-x}Sr_xFeO_3$, $Y_{1-x}Mg_xCrO_3$, $Y_{1-x}Ca_xCrO_3$, $Y_{1-x}Sr_xCrO_3$, $Y_{1-x}Ba_xCrO_3$, $Gd_{1-x}Ca_xCrO_3$, $LaCr_{1-y}Mn_yO_3$, $LaCr_{1-y}Mg_yO_3$, etc. Furthermore, the perovskite-type metal oxides may exhibit metallic electric conductor properties and semiconductor properties by replacing a portion of the metal A or B with another metal in the above general formula. Such perovskite-type metal oxides include, for example, $Gd_{1-x}Sr_xCo_{1-y}Mn_yO_3$, $La_{1-x}Ca_xCr_{1-y}Co_yO_3$, etc. In the above general formula, each of x and y represents a number which is equal to or greater than 0 and less than 1.

[0036] The perovskite-type metal oxide can be produced by mixing an oxide or carbonate of a metal so that the metal is of such an amount as to constitute the oxide stoichiometrically, and then baking the mixture at a predetermined temperature. The produced perovskite-type metal oxide is crushed into a powder having a particle diameter ranging from 0.005 to 0.3 μm, and waster is added to the powder to produce a slurry. The slurry is coated on the surface of the ceramic burner 3 by spraying, dried at a predetermined temperature, and then baked at a predetermined temperature. When thus baked, the particles of the perovskite-type metal oxide have diameters in the range from 0.04 to 5 μm, providing an electrically conductive layer 7 which has a thickness ranging from 10 to 300 μm and uniformly covers the ceramic burner 3.

[0037] When the slurry is baked into the electrically conductive layer 7, the perovskite-type metal oxide and the ceramic burner 3 jointly make up a solid solution. Therefore, the electrically conductive layer 7 is firmly bonded to the ceramic burner 3. As described above, the ceramic burner 3 comprises a porous ceramic plate having surface pores each having a size ranging from 3 to 200 μm. Because the slurry contains the perovskite-type metal oxide powder with the particle diameter ranging from 0.005 to 0.3 μm, the particles of the perovskite-type metal oxide powder uniformly cover the surface of the ceramic plate 3 and enter the surface pores of the ceramic plate. When the particles of the perovskite-type metal oxide powder which have entered the surface pores of the ceramic plate are baked, the produced electrically conductive layer 7 is securely anchored to the ceramic burner 3.

[0038] If the particle diameter of the perovskite-type metal oxide powder were smaller than 0.005 μm, then the particles of the perovskite-type metal oxide powder would enter the surface pores too deeply, failing to produce a electrically conductive layer 7 of uniform thickness. If the particle diameter of the perovskite-type metal oxide powder were greater than 0.3 μm, then when the perovskite-type metal oxide powder is baked, it would not form particles having diameters in the range from 0.04 to 5 μm, failing to securely anchor the electrically conductive layer 7 to the ceramic burner 3.

[0039] The electrically conductive layer 7 may also firmly be bonded to the ceramic burner 3 by roughening the surface of the porous ceramic plate to adjust the surface roughness thereof, rather than adjusting the particle diameter of the perovskite-type metal oxide.

[0040] Inventive Examples of the present invention will be described below.

[Inventive Example 1]

[0041] In Inventive Example 1, $La_{0.7}Sr_{0.3}MnO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0042] A powder of La_2O_3, a powder of $SrCO_3$, and a powder of Mn_2O_3 were mixed at a molar ratio of 0.7 : 0.3 : 1, and 200 g of ethanol was added to the mixture. The mixed components were mixed by a ball mill in a wet process. After the mixture was dried, it was molded by a uniaxial hydraulic press. The molded product was preliminarily baked at 1100°C for 12 hours in an electric furnace, and then crushed into a powder by an automatic mortar in a dry process. The powder was then baked at 1300°C for 12 hours in an electric furnace, and then crushed into a powder by an automatic mortar in a dry process.

[0043] The baked powder was analyzed by an X-ray diffraction process. As a result, it was confirmed that the baked power had an $LaMnO_3$-based crystalline structure.

[0044] To the powder, there were added water of the same weight as the powder and a dispersant (tradename: Seruna D-305 manufactured by Chukyo Yushi) in 0.5 weight % of the powder. The components were mixed by a ball mill in a wet process, and dried into an $La_{0.7}Sr_{0.3}MnO_3$ powder having an average diameter of 0.2 μm. An analysis of the powder with an energy-distributed X-ray analyzer confirmed that the proportions of the constituents of the powder were La : Sr : Mn = 0.7 : 0.3 : 1 (molar ratio).

[0045] To the $La_{0.7}Sr_{0.3}MnO_3$ powder, there were added water in 20 - 50 weight % of the powder and a dispersant (tradename: Seruna D-305 manufactured by Chukyo Yushi) in 0.5 weight % of the powder. The components were mixed into a slurry by a ball mill in a wet process. The slurry was then sprayed onto the surface of a ceramic plate by a commercially available atomizer, producing a film on the surface of the ceramic plate. The film was then dried at 110°C for 2 hours in a drier, and thereafter baked at 1080°C for 1 to 3 hours in an electric furnace. As a result, a ceramic burner 3 having an electrically conductive layer 7 made of $La_{0.7}Sr_{0.3}MnO_3$ with a particle diameter of 2 μm and having a thickness of 110 μm was produced.

[0046] The electrically conductive layer 7 was formed so as to cover the surface of the ceramic burner 3 uniformly with $La_{0.7}Sr_{0.3}MnO_3$. Because particles of $La_{0.7}Sr_{0.3}MnO_3$ entering the surface pores of the ceramic burner 3 were baked, the electrically conductive layer 7 and the ceramic burner 3 were firmly bonded to each other.

[0047] Then, the ceramic burner 3 was installed in the combustion device 3 shown in FIG. 1, and a mixture of a fuel gas and air was supplied to the combustion device 3 and ignited. A voltage of 120 V was applied between the electrically conductive layer 7 and the flame rod 8, and flame currents detected by the flame detector 9 in response to input powers in a predetermined range were measured. The measured flame currents are shown in FIG. 2.

[0048] As can be seen from FIG. 2, with the electrically conductive layer 7 according to Inventive Example 1, the flame detector 9 detected flame currents ranging from 40 to 160 μA with respect to input powers ranging from 8 to 24 kW. Usually, a flame current of 1 μA is needed for the ignition detector 9 to detect an ignition, and a flame current of 0.1 μA is needed for the ignition detector 9 to detect a flame failure. Since the flame currents produced by the electrically conductive layer 7 according to Inventive Example 1 are much greater than 1 μA, they are in a range large enough for the ignition detector 9 to detect an ignition.

[0049] Temperature-dependent changes in the electric conductivity of $La_{0.7}Sr_{0.3}MnO_3$ of the electrically conductive layer 7 are shown in FIG. 3. A review of FIG. 3 reveals that $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1 suffers only small changes in the electric conductivity even at high temperatures, and is hence stable.

[0050] Then, the ceramic burner 3 was installed in the combustion device 3 shown in FIG. 1, and a mixture of a fuel gas and air with an excess air ratio of 1.4 was supplied to the combustion device 3 and ignited. A voltage of 120 V was applied between the electrically conductive layer 7 and the flame rod 8, and flame currents detected by the flame detector 9 in response to input powers in a predetermined range were measured. The measured flame currents are shown in FIG. 4.

[0051] The excess air ratio represents the ratio of an amount of air to be actually mixed with the fuel gas to a theoretical or stoichiometric amount of air, which is assumed to be "1", required for the complete combustion of a given amount of fuel gas. The excess air ratio is indicated as a dimensionless number.

[0052] A ceramic burner 3 (Conventional Example) which was manufactured in the same manner as with Inventive Example 1 except that it had no electrically conductive layer 7 was installed in the combustion device 3 shown in FIG. 1, and flame currents were measured in the same conditions as with Inventive Example 1. Furthermore, a ceramic burner (Comparative Example) made of electrically conductive ceramics of petalite and having no electrically conductive layer 7 was installed in the combustion device 3 shown in FIG. 1, and flame currents were measured in the same conditions as with Inventive Example 1. The measured flame currents are also shown in FIG. 4.

[0053] As can be seen from FIG. 4, the ceramic burner 3 with the electrically conductive layer 7 according to Inventive Example 1 allowed the flame detector 9 to detect flame currents large enough to detect an ignition irrespective of the magnitude of input powers even under such conditions that the excess air ratio is 1.4 and the mixture is air-rich.

[0054] The ceramic burner 3 according to Conventional Example was an electric nonconductor, and did not allow the flame detector 9 to detect almost any flame currents irrespective of the magnitude of input powers. With the ceramic burner 3 according to Comparative Example, under such conditions that the mixture was air-rich and the temperature of the ceramic burner 3 was relatively low, detected flame currents were reduced to the same level as with the ceramic burner 3 according to Conventional Example as the input power was increased.

[0055] The ceramic burner 3 according to Inventive Example 1 was installed in the combustion device 3 shown in FIG. 1, and a supplied mixture was ignited while the excess air ratio and the combustion capability of the combustion device 3 were varied. A voltage of 120 V was applied between the electrically conductive layer 7 and the flame rod 8, and time-dependent changes in flame currents detected by the flame detector 9 were measured. The measured changes are shown in FIGS. 5(a), 5(b), 6(a), and 6(b).

[0056] The ceramic burner 3 according to Conventional Example and the ceramic burner 3 according to Comparative Example were installed in the combustion device 3 shown in FIG. 1, and time-dependent changes in flame currents detected by the flame detector 9 were measured under the same conditions as those with the ceramic burner 3 according to Inventive Example 1. The measured changes are also shown in FIGS. 5(a), 5(b), 6(a), and 6(b).

[0057] Specifically, FIG. 5(a) shows time-dependent changes in flame currents at the time the excess air ratio is 1.4 and the combustion device is set to a maximum combustion capability. In FIG. 5(a), the temperature of the ceramic burner is relatively low. FIG. 5(b) shows time-dependent changes in flame currents at the time the excess air ratio is 1.4 and the combustion device is set to a minimum combustion capability. In FIG. 5(b), the temperature of the ceramic burner is higher than the temperature of the ceramic burner in FIG. 5(a).

[0058] FIG. 6(a) shows time-dependent changes in flame currents at the time the excess air ratio is 1.1, making the mixture gas-rich, and the combustion device is set to a maximum combustion capability. In FIG. 6(a), the temperature of the ceramic burner is higher than the temperature of the ceramic burner in FIG. 5(b). FIG. 6(b) shows time-dependent changes in flame currents at the time the excess air ratio is 1.1 and the combustion device is set to a minimum combustion capability. In FIG. 6(b), the temperature of the ceramic burner is highest.

[0059] It can be understood from FIGS. 5(a), 5(b), 6(a), and 6(b) that the electrically conductive layer 7 according to Inventive Example 1 allowed the flame detector 9 to detect flame currents large enough to detect an ignition within a very short period of time irrespective of burning conditions.

[0060] The ceramic burner 3 according to Conventional Example was an electric nonconductor, and did not allow the flame detector 9 to detect almost any flame currents irrespective of burning conditions, as can be seen from FIGS. 5(a), 5(b), 6(a), and 6(b). With the ceramic burner 3 according to Comparative Example, as can be seen from FIG. 5(a), under such conditions that the temperature of the ceramic burner 3 was relatively low, substantially the same flame currents as those with the ceramic burner 3 according to Conventional Example were detected. As can be seen from FIGS. 5(b), 6(a), and 6(b), the ceramic burner 3 according to Comparative Example allowed the flame detector 9 to detect flame currents sufficiently large to detect an ignition and a flame failure under such conditions that the temperature of the ceramic burner was high. However, it took 0.5 to 2.0 minutes until the flame currents grew large enough for the flame detector 9 to detect.

[0061] The ceramic burner 3 according to Inventive Example 1 was installed in the combustion device 3 shown in FIG. 1, and a voltage of 120 V was applied between the electrically conductive layer 7 and the flame rod 8. Time-dependent changes in flame currents detected by the flame detector 9 were measured when the burning conditions were varied during combustion or at the time the mixture was extinguished after combustion and then re-ignited. The measured changes are shown in FIGS. 7(a) and 7(b).

[0062] The ceramic burner 3 according to Conventional Example and the ceramic burner 3 according to Comparative Example were installed in the combustion device 3 shown in FIG. 1, and time-dependent changes in flame currents detected by the flame detector 9 were measured under the same conditions as those with the ceramic burner 3 according to Inventive Example 1. The measured changes are also shown in FIGS. 7(a) and 7(b).

[0063] FIG. 7(a) shows time-dependent changes in flame currents measured when the mixture was combusted for 15 minutes with an excess air ratio of 1.1 and a minimum combustion capability of the combustion device 1, and then the excess air ratio remained unchanged and the combustion device 1 set to a medium combustion capability. FIG. 7(b) shows time-dependent changes in flame currents measured when the mixture was combusted for 15 minutes with an excess air ratio of 1.1 and a minimum combustion capability of the combustion device 1, and then the mixture was extinguished, the combustion device 1 was completely cooled, and thereafter the mixture was re-ignited with an excess air ratio of 1.1 and a medium combustion capability of the combustion device 1.

[0064] As can be seen from FIGS. 7(a) and 7(b), with the ceramic burner 3 with the electrically conductive layer 7 according to Inventive Example 1, flame currents suffered only a slight overshoot, and normal flame currents were recovered within a very short period of time, irrespective of burning conditions.

[0065] With the ceramic burner 3 according to Comparative Example, however, flame currents exhibited a large overshoot immediately after burning conditions were changed, as shown in FIG. 7(a). The flame currents were out of scale for 4 seconds immediately after the burning conditions were changed. It took 20 to 25 minutes until normal flame currents were restored and stabilized after the overshoot. With the ceramic burner 3 according to Comparative Example, furthermore, immediately after the mixture was extinguished after combustion and then re-ignited, flame currents exhibited a large overshoot, as shown in FIG. 7(b), and it took 20 to 25 minutes until normal flame currents were restored and stabilized after the overshoot. The ceramic burner 3 according to Comparative Example did not allow the ignition detector 9 to detect an ignition until normal flame currents were restored after the overshoot.

[0066] Since the ceramic burner 3 according to Conventional Example is an electric nonconductor, it did not allow the flame detector 9 to detect almost any flame currents irrespective of burning conditions.

[Inventive Example 2]

[0067] In Inventive Example 2, $La_{0.7}Sr_{0.3}MnO_3$ was used as the electrically conductive perovskite-type metal oxide, and the electrically conductive layer 7 contained borosilicate glass as an inorganic binder.

[0068] First, an $La_{0.7}Sr_{0.3}MnO_3$ powder was produced in the same manner as with Inventive Example 1. The borosilicate glass was crushed into a powder by a ball mill in a wet process.

[0069] To the $La_{0.7}Sr_{0.3}MnO_3$ powder, there were added water in 20 - 50 weight % of the powder, a dispersant (tradename: Seruna D-305 manufactured by Chukyo Yushi) in 0.5 weight % of the powder, and the borosilicate glass powder. The components were mixed into a slurry by a ball mill in a wet process. The added amount of the borosilicate glass powder was 4 weight % of the total amount of an electrically conductive layer 7 to be formed from the slurry.

[0070] The slurry was then sprayed onto the surface of a ceramic plate by a commercially available atomizer, producing a film on the surface of the ceramic plate. The film was then dried at 110°C for 2 hours in a drier, and thereafter baked at 950°C for 1 hour in an electric furnace, thus producing an electrically conductive layer 7 having a thickness of 120 μm.

[0071] The electrically conductive layer 7 was formed so as to cover the surface of the ceramic burner 3 uniformly with $La_{0.7}Sr_{0.3}MnO_3$. Because particles of $La_{0.7}Sr_{0.3}MnO_3$ entering the surface pores of the ceramic burner 3 were baked, the electrically conductive layer 7 and the ceramic burner 3 were firmly bonded to each other. The electrically conductive layer 7 contained the borosilicate glass in 4 weight % of the total amount thereof. As a result, the particles of $La_{0.7}Sr_{0.3}MnO_3$ were bonded to each other or to the ceramic burner 3 by the binder of borosilicate glass, bonding the electrically conductive layer 7 and the ceramic burner 3 further firmly.

[0072] Five slurries containing $La_{0.7}Sr_{0.3}MnO_3$ were prepared in the same manner as described above except that the borosilicate glass powder was added in different amounts. Specifically, the borosilicate glass powder was added in 0 weight %, 2 weight %, 4 weight %, 10 weight %, and 20 weight % of the total amount of electrically conductive layers 7 to be formed from the slurries.

[0073] The produced slurries were then sprayed onto the surfaces of ceramic plates by a commercially available atomizer, producing films on the surfaces of the ceramic plates. The films were then dried at 110°C for 2 hours in a drier, and thereafter baked at 880 to 1100°C for 1 to 3 hours in an electric furnace. As a result, ceramic burners 3 having electrically conductive layers 7 having a thickness of 120 pm and containing no borosilicate glass and 2 weight %, 4 weight %, 10 weight %, and 20 weight % of borosilicate glass with respect to the total amount of the electrically conductive layers 7 were produced.

[0074] In order to check ranges of baking temperatures in which the $La_{0.7}Sr_{0.3}MnO_3$ powder bonded to the ceramic burner 3 by baking acts as the electrically conductive layer 7, minimum baking temperatures T_1 for preventing the formed electrically conductive layer 7 from being peeled off and temperatures T_2 at which the resistance of the electrically conductive layer 7 is infinitely large were measured. These measured temperatures T_1, T_2 and ranges d of the baking temperatures ($d = T_2 - T_1$) are shown in Table 1 below.

[0075] Changes in the resistance of the electrically conductive layers 7 which contained 0 weight %, 2 weight %, 4 weight %, 10 weight %, and 20 weight % of the total amount of electrically conductive layers 7, with respect to the baking temperatures are shown in FIG. 8.

Table 1

Added amount (wt %)	T_1	T_2	d
0	1060	1100	40
2	880	1000	120
4	880	990	110
10	880	970	90
20	880	920	40

[0076] As can be seen from Table 1 and FIG. 8, adding the borosilicate glass is effective to lower the minimum baking temperature at which the $La_{0.7}Sr_{0.3}MnO_3$ powder can be baked and increase the range of baking temperatures at which the baked $La_{0.7}Sr_{0.3}MnO_3$ powder acts as the electrically conductive layer 7. Therefore, it is made easy to establish a desired baking temperature.

[0077] Insofar as the content of the borosilicate glass is in the range from 1 to 20 weight % of the total amount of the electrically conductive layer 7, the resistance of the electrically conductive layer 7 can be controlled by appropriately establishing a desired baking temperature. If the content of the borosilicate glass exceeded 20 weight % of the total amount of the electrically conductive layer 7, then the resistance of the electrically conductive layer 7 would become excessive regardless of the baking temperature.

[0078] In Inventive Example 2, borosilicate glass was used as the inorganic binder. However, soda lime glass may also be used as the inorganic binder to obtain the same advantages as described above.

[Inventive Example 3]

[0079] In Inventive Example 3, $La_{0.7}Sr_{0.3}FeO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0080] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that an Fe_2O_3 powder was used instead of the Mn_2O_3 powder in Inventive Example 1.

[0081] The ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}FeO_3$ according to Inventive Example 3 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1.

[Inventive Example 4]

[0082] In Inventive Example 4, $La_{0.5}Sr_{0.5}CoO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0083] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that a powder of La_2O_3, a powder of $SrCO_3$, and a powder of Co_3O_4 were mixed at a molar ratio of 0.5 : 0.5 : 1, and the powder was baked at a temperature of 1200°C after the preliminary baking.

[0084] The ceramic burner 3 having the electrically conductive layer 7 with $La_{0.5}Sr_{0.5}CoO_3$ according to Inventive Example 4 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1.

[Inventive Example 5]

[0085] In Inventive Example 5, $La_{0.5}Ca_{0.5}CrO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0086] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that a powder of La_2O_3, a powder of $CaCO_3$, and a powder of Cr_2O_3 were mixed at a molar ratio of 0.5 : 0.5 : 1, and the powder was baked at a temperature of 1500°C after the preliminary baking.

[0087] The ceramic burner 3 having the electrically conductive layer 7 with $La_{0.5}Ca_{0.5}CrO_3$ according to Inventive Example 5 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1.

[Inventive Example 6]

[0088] In Inventive Example 6, $La_{0.6}Sr_{0.4}CrO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0089] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that a powder of La_2O_3, a powder of $SrCO_3$, and a powder of Cr_2O_3 were mixed at a molar ratio of 0.6 : 0.4 : 1, and the powder was baked at a temperature of 1500°C after the preliminary baking.

[0090] The ceramic burner 3 having the electrically conductive layer 7 with $La_{0.6}Sr_{0.4}CrO_3$ according to Inventive Example 6 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1.

[Inventive Example 7]

[0091] In Inventive Example 7, $La_{0.2}Ca_{0.8}MnO_3$ was used as the electrically conductive perovskite-type metal oxide.

[0092] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that a powder of La_2O_3, a powder of $CaCO_3$, and a powder of Mn_2O_3 were mixed at a molar ratio of 0.8 : 0.2 : 1.

[0093] The ceramic burner 3 having the electrically conductive layer 7 with $La_{0.2}Ca_{0.8}$ MnO_3 according to Inventive Example 7 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example

1.

[Inventive Example 8]

[0094] In Inventive Example 8, $Gd_{0.8}Sr_{0.2}Co_{0.9}Mn_{0.1}O_3$ was used as the electrically conductive perovskite-type metal oxide.

[0095] A ceramic burner 3 having an electrically conductive layer 7 was manufactured in exactly the same manner as with Inventive Example 1 except that a powder of Gd_2O_3, a powder of $SrCO_3$, a powder of Co_3O_4, and a powder of Mn_2O_3 were mixed at a molar ratio of 0.6 : 0.4 : 1, and the powder was baked at a temperature of 1500°C after the preliminary baking.

[0096] The ceramic burner 3 having the electrically conductive layer 7 with $Gd_{0.8}Sr_{0.2}Co_{0.9}Mn_{0.1}O_3$ according to Inventive Example 8 was installed in the combustion device 1 shown in FIG. 1. Flame currents sufficiently large to detect an ignition between the electrically conductive layer 7 and the flame rod 8 were obtained as with the ceramic burner 3 having the electrically conductive layer 7 with $La_{0.7}Sr_{0.3}MnO_3$ according to Inventive Example 1.

[0097] Although certain preferred embodiments of the present invention has been shown and described in detail, it should be understood that various changes and modifications may be made therein without departing from the scope of the appended claims.

Claims

1. A combustion device comprising:

    a ceramic burner comprising a porous ceramic plate having a plurality of burner ports defined therein;
    an electrically conductive layer disposed on a surface of said ceramic burner where flames are produced;
    an electric conductor disposed in facing relation to said electrically conductive layer; and
    ignition detecting means for detecting a flame current flowing through the flames to detect an ignition when a voltage is applied between said electrically conductive layer and said electric conductor;
    said electrically conductive layer being made of an electrically conductive perovskite-type metal oxide.

2. A combustion device according to claim 1, wherein said electrically conductive layer uniformly covers the surface of said porous ceramic plate, said electrically conductive perovskite-type metal oxide entering surface pores in said ceramic plate.

3. A combustion device according to claim 1, wherein said electrically conductive layer comprises particles of the electrically conductive perovskite-type metal oxide which have diameters ranging from 0.04 to 5 μm.

4. A combustion device according to claim 1, wherein said electrically conductive layer has a thickness ranging from 10 to 300 μm.

5. A combustion device according to claim 1, wherein said electrically conductive layer contains an inorganic binder ranging from 1 to 20 weight % of the total amount thereof, said electrically conductive layer being bonded to said porous ceramic plate by said inorganic binder.

6. A combustion device according to claim 1, wherein said electrically conductive perovskite-type metal oxide is represented by $La_{1-x}Sr_xMnO_3$ where x represents a number which is equal to or greater than 0 and less than 1.

FIG.1

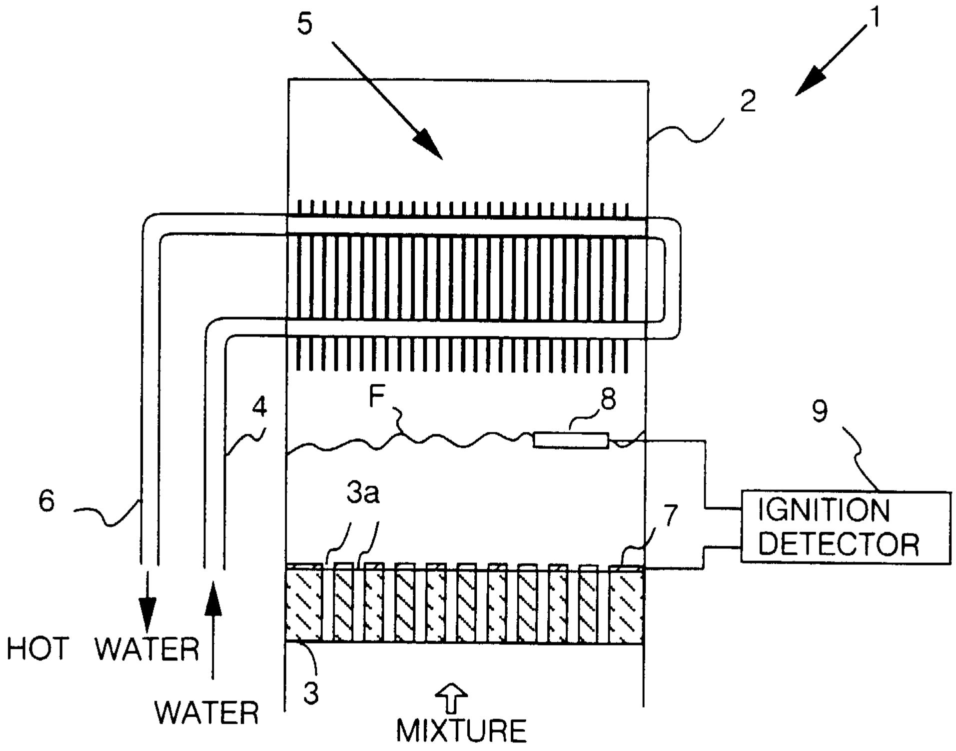


FIG.2

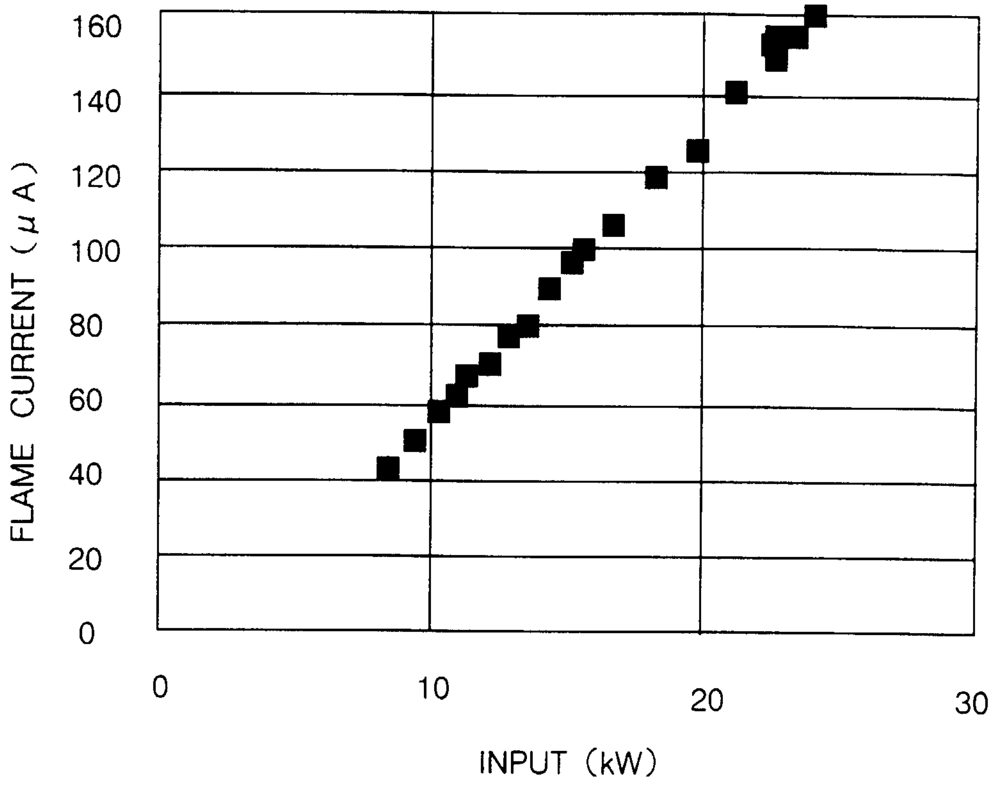


FIG.3

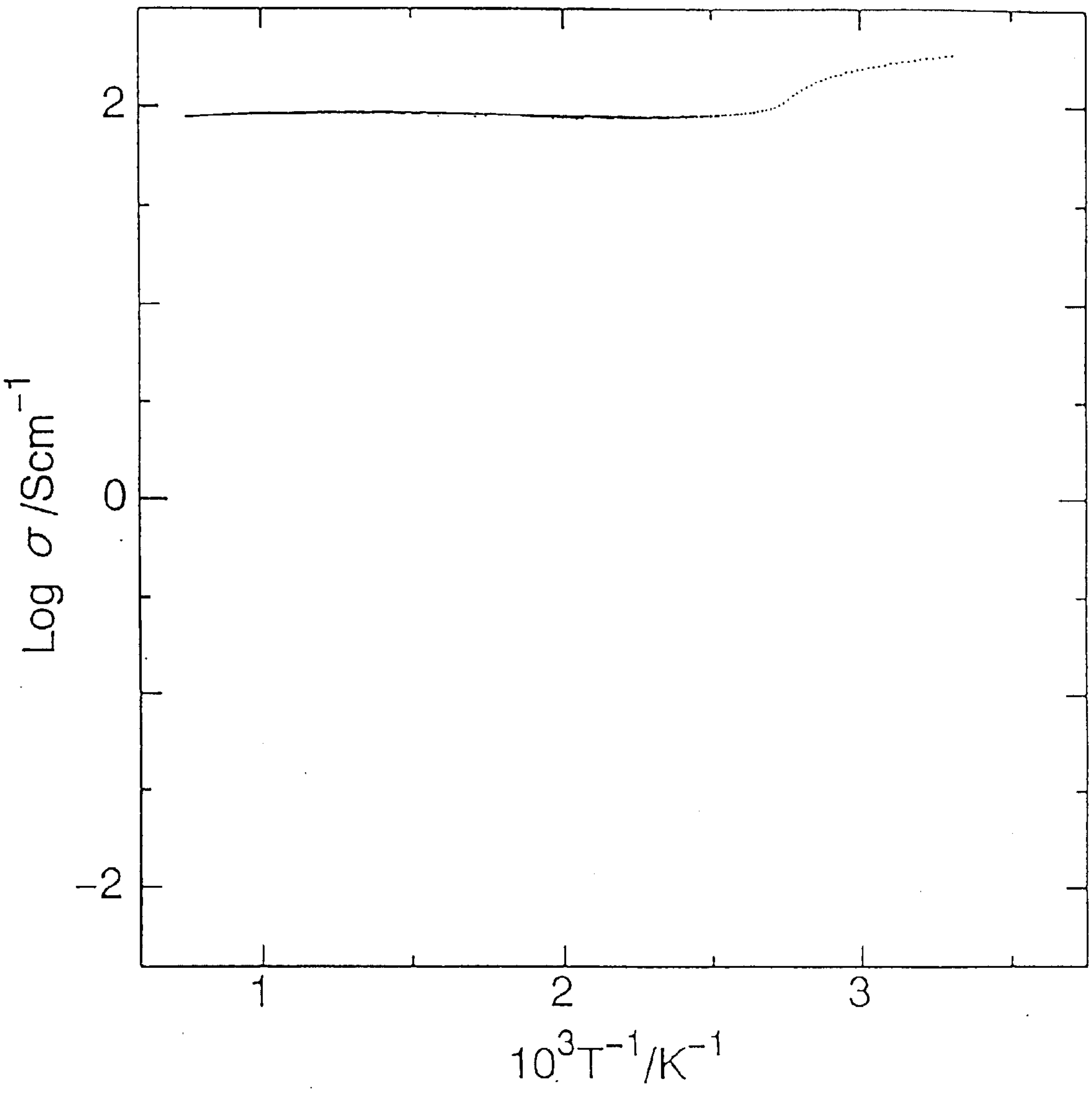


FIG.4

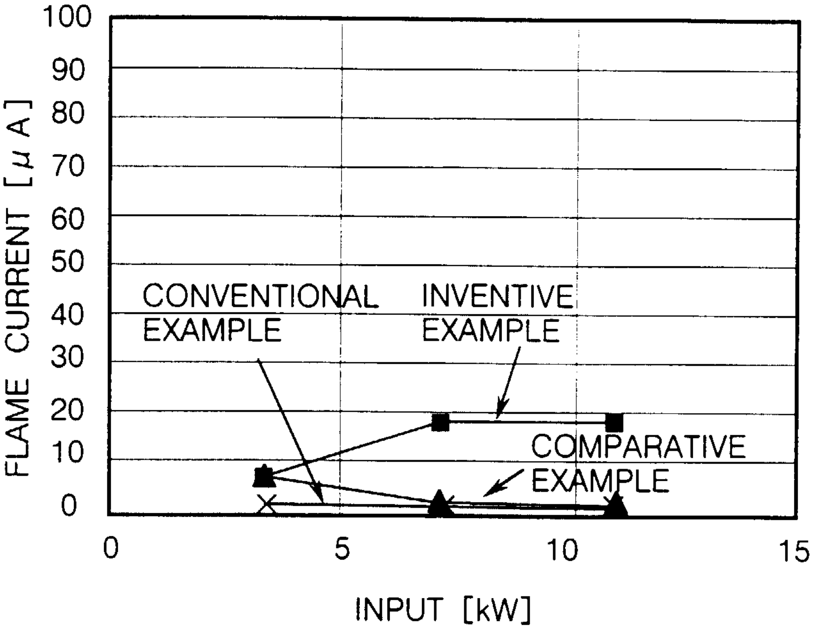

100
90
80
70
60
50
40
30
20
10
0
FLAME CURRENT [μA]
0
5
10
15
INPUT [kW]
CONVENTIONAL EXAMPLE
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE

FIG.5(a)

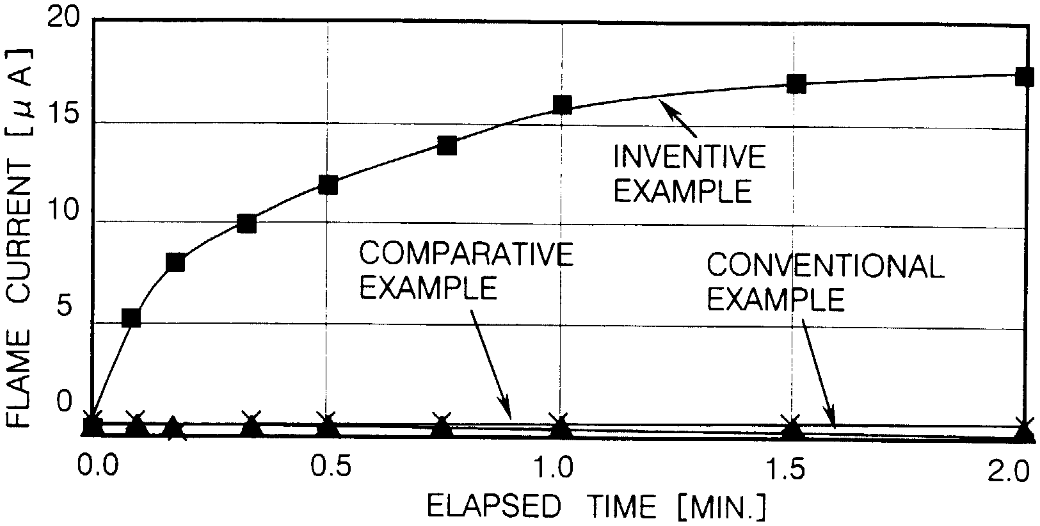

FLAME CURRENT [μA]
20
15
10
5
0
0.0
0.5
1.0
1.5
2.0
ELAPSED TIME [MIN.]
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE
CONVENTIONAL EXAMPLE

FIG.5(b)

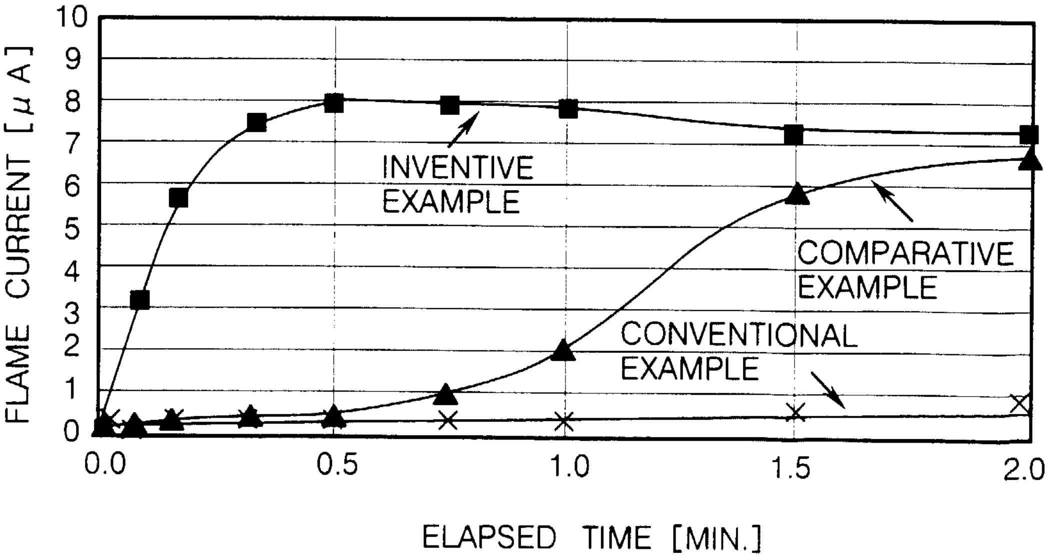

FLAME CURRENT [μA]
10
9
8
7
6
5
4
3
2
1
0
0.0
0.5
1.0
1.5
2.0
ELAPSED TIME [MIN.]
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE
CONVENTIONAL EXAMPLE

FIG.6(a)

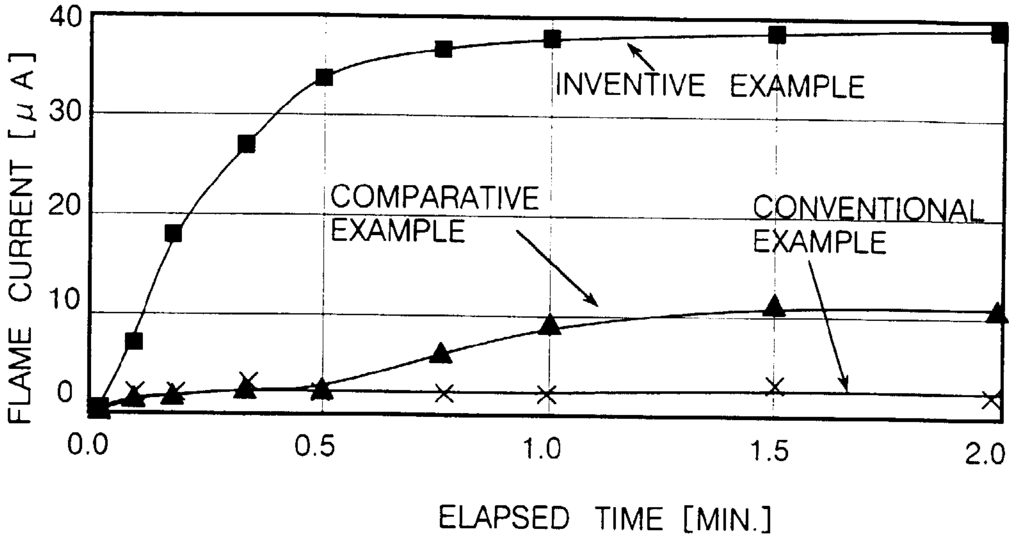

FLAME CURRENT [μA]
40
30
20
10
0
0.0
0.5
1.0
1.5
2.0
ELAPSED TIME [MIN.]
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE
CONVENTIONAL EXAMPLE

FIG.6(b)

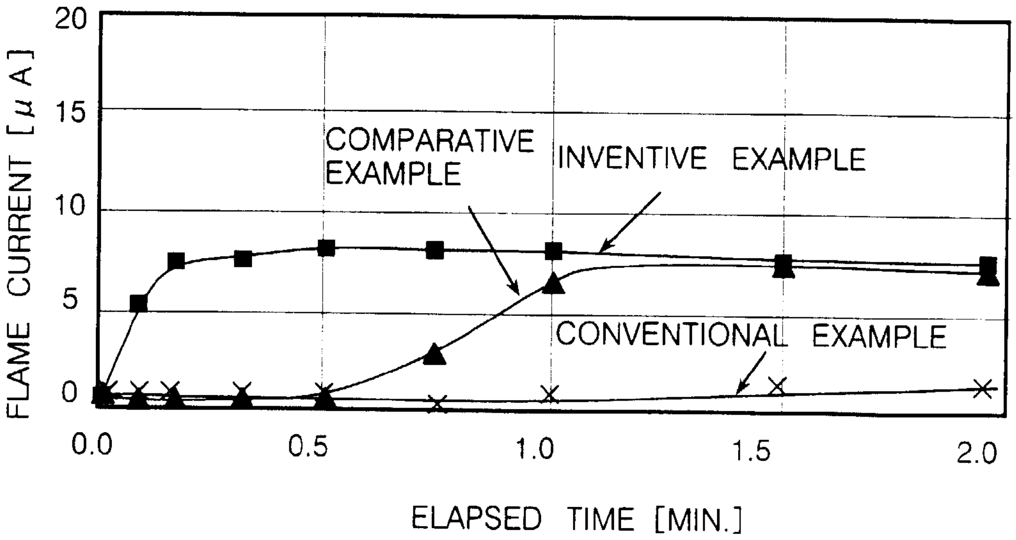

FLAME CURRENT [μA]
20
15
10
5
0
0.0
0.5
1.0
1.5
2.0
ELAPSED TIME [MIN.]
COMPARATIVE EXAMPLE
INVENTIVE EXAMPLE
CONVENTIONAL EXAMPLE

FIG.7(a)

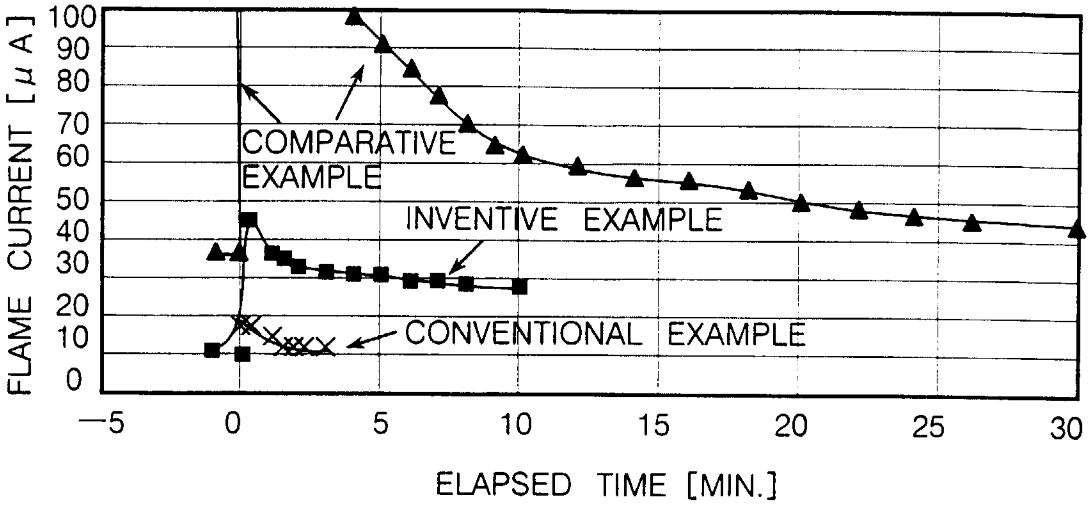

FLAME CURRENT [μA]
100
90
80
70
60
50
40
30
20
10
0
COMPARATIVE EXAMPLE
INVENTIVE EXAMPLE
CONVENTIONAL EXAMPLE
—5
0
5
10
15
20
25
30
ELAPSED TIME [MIN.]

FIG.7(b)

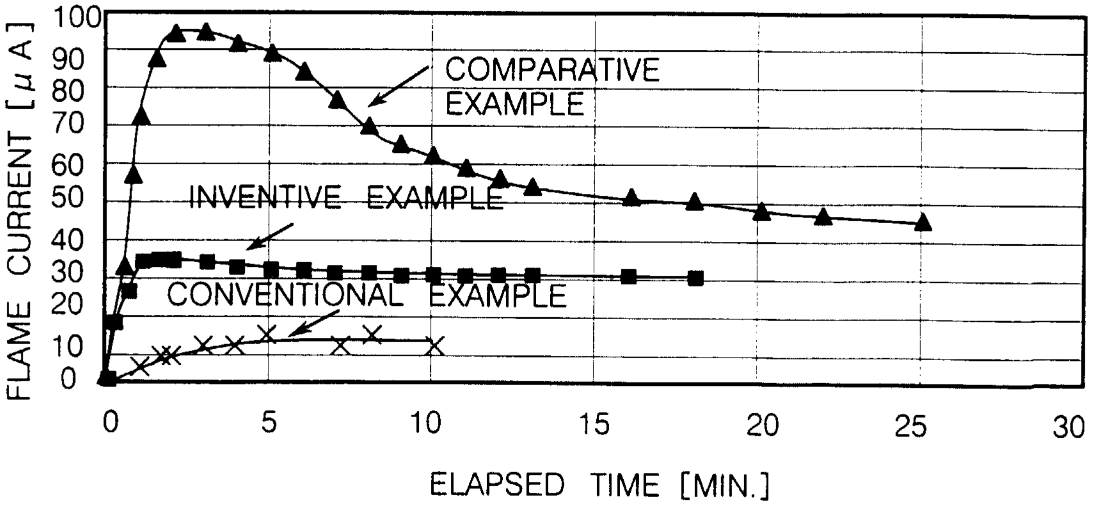
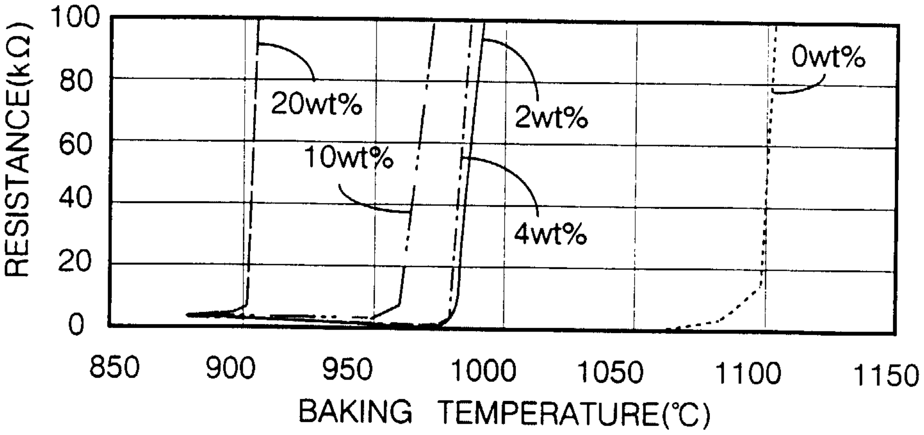

FLAME CURRENT [μA]
100
90
80
70
60
50
40
30
20
10
0
COMPARATIVE EXAMPLE
INVENTIVE EXAMPLE
CONVENTIONAL EXAMPLE
0
5
10
15
20
25
30
ELAPSED TIME [MIN.]

FIG.8


RESISTANCE(kΩ)
100
80
60
40
20
0
850
900
950
1000
1050
1100
1150
BAKING TEMPERATURE(℃)
20wt%
10wt%
2wt%
4wt%
0wt%