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CATALYTIC RADIANT HEATER

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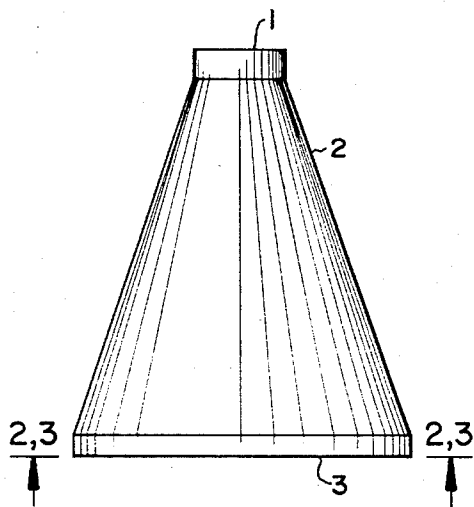


FIG. 1

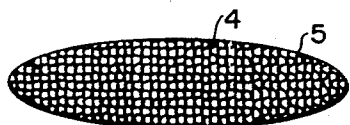


FIG. 2

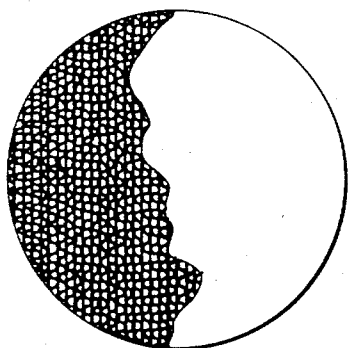


FIG. 3

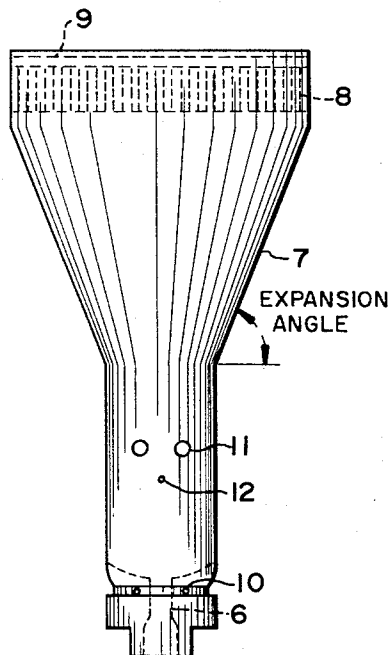


FIG. 4



FIG. 5

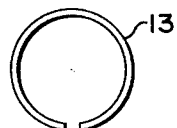


FIG. 6

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## CATALYTIC RADIANT HEATER

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9 Claims

### ABSTRACT OF THE DISCLOSURE

This disclosure concerns heaters which utilize a fuel, generally gaseous in nature, and an oxygen-containing gas such as air. The fuel and oxidizing gas are combined catalytically and burn without flame formation at the surface of a non-combustible unitary ceramic skeletal block with gas flow channels. The devices are useful as heaters when the temperature of this surface is sufficiently high by virtue of the combustion to cause emission of substantial amounts of heat by radiation.

### BACKGROUND OF THE INVENTION

This invention pertains to new types of devices for emitting heat by radiation. More particularly, it relates to heaters comprising precious metal catalysts which produce flameless combustion and provide radiant infrared energy. These heaters use unitary channeled ceramic blocks to assist in the oxidation. These devices are useful for removing paint, varnish and the like, installing and removing asphalt tile, baking and drying painted surfaces, heating and radiating greenhouses, and other purposes.

Catalytic heaters which utilize a precious metal catalyst such as a platinum black on substrate such as asbestos fiber or cloth are known. Such heaters are generally bulky, depend on secondary air for combustion, and require a large flame for ignition. Moreover, the combustion gases tend to flow unevenly to the surface of such heaters. Uneven burning and hot spots result causing a decrease in the catalyst life. This uneven burning also produces unoxidized or partially oxidized combustion products thereby providing inefficient operation and poisonous carbon monoxide emission. Other infrared energy producing heaters which use ceramic gas flow channels are known, but these heaters are not capable of using a broad range of air-fuel mixtures. Nor are they capable of providing a large turn-down ratio. Turn-down ratio refers to ability to decrease the rate of fuel consumption by decreasing fuel flow. This reduction automatically reduces the air input. A turn-down ratio of 100:1 means a fuel may be consumed at a maximum rate in a burner as well as  $\frac{1}{100}$  this maximum rate. This turn-down feature is very desirable when the catalytic heater is called upon to perform various jobs, each requiring quite different heating requirements.

### SUMMARY OF THE INVENTION

The present invention pertains to catalytic radiant heaters which use simple venturi means to provide air for combustion and assist in distributing the combustion mixture, and a unitary ceramic block support with multiple gas passages, on the surface of which are deposited a platinum group metal and preferably a refractory metal oxide. The catalytic support assists in catalyzing the oxidation of the fuel, preventing combustion flashback, and radiating heat to the object to be heated.

It is an object of this invention to provide a catalytic heater which provides for complete combustion of fuel. It is a further object to provide a device which prevents

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loss of catalyst life due to creation of hot spots during operation. A still further object is provision of a catalytic heater simple in design which provides a broad range of usable air-fuel ratios as well as a large turn-down ratio and variation in B.t.u. availability. Other objects will be apparent from the following detailed description.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is an elevational view of a housing of a catalytic heater of this invention.

FIGURE 2 represents a plan view of a catalyst block, showing an embodiment which is shaped to be encased in the face of the housing of FIGURE 1, where the face of the housing is in an elliptical shape.

FIGURE 3 is a plan view of a fragment of a catalyst block encased in the face of the housing of FIGURE 1, where the face of the housing is in a circular shape.

FIGURE 4 is an elevational view of an embodiment of a catalytic heater unit of this invention showing the catalyst block encased in the face of a conical housing the primary air inspirators, the venturi, and the angle between the housing and a plane normal to the conic axis of the housing.

FIGURE 5 is a side view of a slip ring which can be used to regulate the inflow of air at apertures 11.

FIGURE 6 is a top view of the slip ring of FIGURE 5.

### DESCRIPTION OF PREFERRED EMBODIMENTS

The catalytic heaters with which this invention is concerned comprise a housing which is of such configuration as to have a larger opening or face and a smaller opening used as a gas inlet port. The cross-sectional area within the housing will generally increase from the smaller to the larger opening and will therefore be adapted to permit expansion of the hot gases therein. A generally smooth transition from smaller to larger opening is preferred, such as in a conical shape, so as to permit efficient expansion and even distribution of the combustion mixture within the housing. The fuel and oxygen-containing gas is fed to the housing at the inlet port through a venturi arrangement. This combustible mixture may optionally be distributed throughout the interior of the housing by use of an inverted cone, a screen, or the like. The gaseous mixture is preferably fed axially into the housing. Either air or the fuel may be fed to the venturi to inspire the other. Air under pressure is preferably used to obtain combustion mixtures having greater than twice the stoichiometric amount of air.

It has been learned that when a conical housing is utilized, particular expansion angles are preferred in order to provide the least amount of irregular heating of the supported catalyst and prolong catalyst life. Expansion angle, as used herein, refers to the angle between the conic surface and the normal to the conic axis in the plane containing the conic axis and its normal. An expansion angle of about 20°–80° is preferred.

The unitary ceramic block support used in connection with this invention is located in the cross-sectional area of the face of the housing and may occupy approximately all of this area. The ceramic may be used in many configurations, e.g. round, square, conical, spherical, and it may be raised or partially raised or recessed from the surface of the housing.

The unitary inert refractory skeletal structure support for the catalyst useful according to this invention is characterized by having a large plurality of unobstructed gas flow channels or paths extending therethrough in the direction of gas flow. The gas flow channels can be one or more of a variety of cross-sectional shapes and sizes. The channels can be of the cross-sectional shape, for example, of the shape of a trapezoid, rectangle, square, sinusoid, or circle so that cross-sections of the support represent a

pattern that can be described as a honeycomb, corrugated or lattice structure.

The meramic support is constructed of a substantially chemically and catalytically inert, porous, rigid, solid refractory material capable of maintaining its shape and strength at high temperatures, for instance up to about 1,100° C. or more. It preferably has a low thermal coefficient of expansion which is less than  $6 \times 10^{-6}$  per °C. between 30° C. and 700° C., this being of importance for good shock resistance. The refractory material has a bulk density of about 0.4–2.0 grams per cubic centimeter, preferably about 0.5–1.5 grams per cubic centimeter and is unglazed and essentially entirely crystalline in form and marked by the absence of any significant amount of glassy or amorphous matrices, for instance of the type found in porcelain materials. Further, the skeletal structure has considerable accessible porosity as distinguished from the substantially non-porous porcelain utilized for electrical applications, for instance spark plug manufacture, characterized by having relatively little accessible porosity. The accessible pore volume not including the volume of the gas flow channels is generally in excess of about 0.01 cubic centimeter per gram of skeletal structure, preferably between about 0.03 and 0.3 cc./g.

The walls of the channels of the unitary ceramic support structures used according to this invention contain a multiplicity of surface macropores in communication with the channels to provide a considerably increased accessible catalyst surface, and a substantial absence of small pores for high temperature stability and strength. Whereas the superficial surface area of such structures may be of the order of about 0.001 to 0.01 m.<sup>2</sup>/g. including the channels, the total surface area is typically many times greater, so that much of the catalytic reaction may take place in the large pores. Typically the total accessible surface area of the support is between about 0.1 and 2.0 m.<sup>2</sup>/g. The skeletal structure has a macropore distribution such that over 95% of the pore volume is in pores having a diameter greater than about 200 Angstrom units.

The total geometric or apparent surface area of the carrier including the walls of the gas flow channels will often be about 0.5 to 12, preferably 1 to 7 square meters per liter of support. The channels through the ceramic support can be of any shape and size consistent with the desired superficial surface and should be large enough to permit free passage of the combustible gas mixture therethrough. The channels may be parallel or generally parallel and extend through the support from one side to an opposite side, such openings being separated from one another by preferably thin walls defining the openings. Alternatively, a network of channels may permeate the body to form a tortuous gas flow path through the ceramic. The channel inlet openings are distributed across the entire face or cross-section of the support. The preferred ceramic supports used in the catalytic heaters of this invention are of zircon-mullite, mullite, mullite-silica, alpha alumina, alumina-silica-magnesia and zirconium silicate. Examples of other refractory crystalline ceramic materials utilizable in place of the preferred materials as support or carrier are sillimanite, magnesium silicates, zircon, petalite, spodumene, cordierite, and alumina-silicates.

Refractory metal oxide is deposited on the porous unitary ceramic support as a continuous thin deposit or as discontinuous thin deposits preferably of thickness of about 0.0004" to 0.001". This catalytic material is a calcined refractory metal oxide which itself is characterized by a porous structure and which possesses a large internal pore volume and total surface area. Generally, the total surface area of the refractory metal oxide is at least about 10 square meters/gram, preferably at least about 100 square meters/gram. Such oxides can be prepared by dehydrating preferably substantially completely the hydrate form of the oxide by calcination usually at

temperatures of about 10° C. to 800° C. The preferred active metal oxides contain members of the gamma or activated alumina family which can be prepared, for instance, by precipitating a hydrous alumina gel and thereafter drying and calcining to expel hydrated water and provide the active gamma-alumina. A particularly preferred active refractory metal oxide is obtained by drying and calcining at temperatures of about 300° C. to 800° C. a mixture of precursor hydrous alumina phases predominating in crystalline trihydrate, that is, containing in excess of about 50% of the total alumina hydrate composition, preferably about 65%–95%, of one or more of the trihydrate forms gibbsite, bayerite and nordstrandite by X-ray diffraction. The substantial balance of the hydrate, preferably about 35% to 5%, may be amorphous hydrous or monohydrous boehmite alumina. Calcination of the precursor hydrous alumina is preferably controlled so that the gamma-alumina obtained contains monohydrate alumina in an amount substantially equivalent to that originally present in the mixture of the high trihydrate precursor hydrous alumina phases. Other suitable catalytic refractory metal oxides include for example active or calcined beryllia, zirconia, magnesia, silica, etc., and combinations of metal oxides such as boron-alumina, silica-alumina, thorium-alumina, etc. Preferably the activated refractory oxide is composed predominantly of oxides of one or more metals of Groups II, III and IV having atomic numbers not exceeding 40. The active refractory metal oxide deposit may constitute about 10 to 300 grams per liter of the ceramic support, preferably about 30 to 120 grams per liter.

Depositing the active refractory metal oxide on the support may be accomplished in several ways. One method involves dipping the support into a solution of the salt of the refractory metal and calcining to decompose the salt to the oxide form. A more preferred method comprises dipping the support into an aqueous suspension, dispersion or slurry of the refractory oxide itself, drying and calcining. In this method, suspensions or dispersions having a solids content in range of about 10% to 70% by weight can be used to deposit a suitable amount of an active refractory metal oxide on the support in a single application. In order to prepare a catalyst having 10% activated alumina on a zircon-mullite structure, about 20%–40% solids in the suspension is used. The percent solids is determined on an ignited weight basis (ignited at 1,100° C.). In general, calcining temperatures within the range of about 150° C. to 800° C. are employed. The calcination is favorably conducted in air, for example flowing dried air, or may be carried out in contact with other gases such as oxygen, nitrogen, hydrogen, flue gas, etc. or under vacuum conditions. The refractory oxide is deposited on the surfaces of the skeletal structure including the channel surfaces and the surfaces of the superficial macropores in communication with the channel surfaces as thin deposits in an amount, by weight, of about 1% to 50% and preferably 5% to 30% based on the weight of the skeletal structure.

The gas flow channels of the unitary ceramic supported catalyst herein are thin-walled channels providing a large amount of superficial surface area. The walls of the cellular channels are generally of the minimum thickness necessary to provide a strong unitary body. This wall thickness will usually fall in the range of about 2 to 10 mils. with this wall thickness the structures contain from about 25–2,500 or more gas or flow channel inlet openings per square inch and a corresponding number of the gas flow channels, preferably about 100–2,000 gas inlet and flow channels per square inch. The open area should be in excess of 60% of the total area. The size and dimensions of the ceramic support useful according to this invention can be varied widely as desired.

The catalyst supports providing the multiplicity of gas flow channels can be prepared from any of the refractory ceramic materials previously mentioned herein. One

method of preparing such supports is by applying by spraying, dipping or brushing a suspension of the pulverized ceramic material and an organic binder, for instance gum arabic, colophony, acrylate resins, methacrylate resins, alkyl resins, phenolic resins or a chlorinated paraffin, to each side of a plurality of flexible organic carrier sheets, for instance of cellulose, acetate paper, onion skin paper, nylon cloth or polyethylene film. Several of the thus-coated carrier sheets are then corrugated by, for instance crimping or multi-folding the sheets, and the remaining coated carrier sheets are left in their original flat condition. The coated corrugated and flat sheets are then superposed one on another in alternate corrugated and flat sheet relationship. The resultant multi-layer structure is then fired in a furnace at a slow rate to prevent breakage due to thermal shock and to a temperature sufficiently high to sinter the ceramic particles into a unitary structure. During the firing the organic binders are removed by decomposition and volatilization. Such preparation method is disclosed in British Patent 882,484. The porous inert unitary solid refractory skeletal structure support having the plurality of gas flow channels is also obtained in commerce from the Minnesota Mining and Manufacturing Company who supplies the supports with 7 and 11 "corrugations" per linear inch. The platinum group metal, for example platinum or palladium, may be deposited on the support so that the supported catalyst may contain about 0.1%–10% metal and preferably 0.05–2% metal based on the total weight of the catalyst plus support. The catalytic metal is preferably deposited directly on the refractory metal oxide activated carrier.

Application of the catalytic metal to the ceramic support can be effected by immersing the skeletal structure, preferably with the refractory metal oxide deposited thereon, in an aqueous solution of a water-soluble inorganic salt or salts of the particular metal or metals, followed by agitating the mixture and precipitating the metal or metals typically in chemically combined state, for instance as oxides, on the skeletal structure. The metal oxide can then be reduced, when the metal form catalyst is desired, by contacting same with a reducing gas, e.g.  $H_2$ , at an elevated temperature of between about 100° and 1,100° C.

Catalytic heaters having radiating catalyst surfaces of about 1 to 8 inches in its greatest dimension are conveniently prepared although larger units using a plurality of unitary supports may also be used. For most purposes and to prevent the need for internal supports, dimensions of about 2 to 4 inches are preferred. The depth of the honeycomb catalyst can be about one inch or more but depths of less than  $\frac{1}{2}$ " and more than  $\frac{1}{16}$ " are quite satisfactory. Depths of about  $\frac{1}{4}$ " have been found particularly satisfactory and are generally preferred.

The fuels used by the catalytic heaters of this invention may be a gas, a vapor, atomized liquid or the like and may comprise volatile hydrocarbons including straight chain hydrocarbons such as lower alkanes, e.g. ethane, propane, butane, heptane and the like. Other usable fuels include aromatics such as benzene, cycloparaffins such as cyclohexane, acetylene, alcohols such as lower alkanols, e.g. methanol, ethanol, isopropanol, and the like.

These fuels may be mixed with air or oxygen-containing gas in a wide range of oxygen-fuel ratios. Generally, at least stoichiometric amounts of oxygen are preferred—and amounts of 0.2 to 20 times the stoichiometric amount are also effectively utilized. Preferably, about 1.05 to 3 times the stoichiometric amount of oxygen is desired. This is a particularly advantageous feature of this invention. An amount of oxidant such as air may be used in accordance with the present invention which would subject known catalytic heaters to flash-back when little oxidant is used, and to flame lifting and extinction when large amounts of oxidant are used, e.g. 2 times the stoichio-

metric amount, especially when the oxidizing surface is exposed to a slight cross-wind. The present radiant heaters of the invention have been exposed to air velocities of 40 m.p.h. across the face of the ceramic block with no flash-back.

These novel and new radiant heaters generally are best started by using less than the normal operational amounts of oxidant. This permits very rapid increase in temperature of the cold catalyst. Once operating temperature is approached, the amount of oxidant may be adjusted to provide the desired oxidant-fuel ratio.

The unique flameless catalytic heater of this invention has still a further desirable feature—that of being self-igniting when a combustible mixture is supplied, even up to about four minutes after the heater has been turned off. This is due to heat retention by the catalyst support and the very high activity of the catalyst. This feature makes utilization of this heater very simple and convenient during applications, requiring its intermittent use.

As earlier mentioned, the turn-down ratio of these heaters is very broad, in the range of about 100:1. This is substantially greater than that for other flameless heaters. This feature permits use of a single heater for one application requiring heating with a device using only about 15 B.t.u./in.<sup>2</sup> as well as for a second application requiring heater capacity of 1,500 B.t.u./in.<sup>2</sup>.

Referring to the drawings: In FIGURE 1 the housing 2 has an inlet port 1 and a face 3. Face 3 is an opening which has a ceramic catalyst block therein. This ceramic catalyst block fills virtually the entire cross-sectional area of the opening and accordingly generally conforms to the shape of this face. FIGURES 2 and 3 represent two of the various shapes which the cross-sectional area of the housing and the ceramic catalyst block therein may be. The ceramic catalyst block has parallel channels 4 disposed in the direction of gas flow and has catalyst 5 deposited thereon. The catalyst block may be retained in the housing by any suitable means. FIGURE 4 shows the ceramic catalyst block 8 held in place in the face of the housing 7 by ring 9, which is biased against the inner wall of the housing. Apertures 10 and 11 are sources of air inspiration into the housing. Venturi 6 is the port of entry for the fuel. Either fuel or air may be fed to the venturi 6 to inspire the other. Pin 12 is used for temporarily retaining slip ring 13 shown in FIGURES 5 and 6, in order to limit the inflow of air through apertures 11.

In operation of the embodiment shown in FIGURE 4, for example, a gaseous fuel, e.g. propane, under pressure is fed to venturi 6 causing inspiration of the oxidant gas, e.g. air. The fuel and air, mixed in the venturi, pass into the housing 7 and ignite at the ceramic catalyst block 8. Additional air is inspired through apertures 11. When igniting a cold burner, slip ring 13 is preferably mounted on pin 12 in order to limit inflow of air through apertures 11.

It should be understood that although this invention has been described with reference to particular embodiments thereof, changes and modifications may be made which are within its intended scope, and it should be limited only by the language of the appended claims.

What is claimed is:

1. A catalytic heater unit for supplying radiant heat having a turn-down ratio of about 100 to 1, and capable of using 0.2 to 20 times the stoichiometric amount of oxygen comprising:

- (a) a housing having a gas inlet port and a face,
- (b) venturi means adjacent to the gas inlet port for supplying a mixture of fuel and an oxygen-containing gas into the housing,
- (c) a catalytic burner-radiator block mounted within the face comprising

- (1) a unitary ceramic block support with channels directing the gas flow therethrough, said ceramic

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block having an open area in excess of 60% of the total area,

(2) a refractory metal oxide having a total surface area of at least about 10 square meters/gram deposited on the support, and

(3) a platinum group metal deposited on the refractory metal oxide whereby said catalytic burner block permits efficient combustion, ready self ignition of the fuel, and resistance to flash-back.

2. A catalytic heater unit according to claim 1 wherein the unitary ceramic block support contains 25-2,500 flow channel inlet openings per square inch.

3. A catalytic heater unit according to claim 2 wherein the refractory metal oxide is alumina and the platinum group metal is platinum.

4. A catalytic heater unit according to claim 3 wherein the catalytic burner-radiator block is comprised of a unitary ceramic block support of about 1 to 8 inches in its greatest dimension and  $\frac{1}{16}$  to 1 inch in depth, whereby the block permits ready self-ignition of the fuel and resistance to flash-back.

5. A catalytic heater unit according to claim 1 wherein the housing is of generally frusto-conical configuration.

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6. A catalytic heater unit according to claim 5 wherein the expansion angle of the housing is about 20° to 80°.

7. A catalytic heater unit according to claim 6 wherein the platinum is deposited to the extent of 0.05 to 10% by weight based on the total weight of the catalyst plus support.

8. A catalytic heater unit according to claim 1 having means for restricting the flow of oxygen into the housing during initial ignition.

9. A catalytic heater unit according to claim 1 wherein the refractory metal oxide deposit has a surface area of at least about 100 square meters/gram.

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