[Second Edition.]

PATENT SPECIFICATION

Convention Date (United States): Aug. 23, 1926. **276,300**

Application Date (in United Kingdom): March 10, 1927. No. 6738/27.

Complete Accepted: Aug. 10, 1928.

8915

COMPLETE SPECIFICATION.

Improvements in and relating to Combustion with the Aid of a Catalyst.

I, THEODORE WILLIAM GRUETTER, a citizen of the United States of America, of Grants Pass, Oregon, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to combustion processes with the aid of catalytic substances.

It has been known for many years that the catalytic power of accelerating combustion is possessed by the platinum-group metals. A standard test for platinum depends on what is called the "glow reaction". The glow reaction consists in absorbing a solution of the metal to be tested into a strip of asbestos, drying, and holding it in a gas flame until incandescent. The gas flame is then extinguished and the gas turned on again on the asbestos strip while it is still warm. Under these conditions it will glow with incandescence if platinum is present. While attempting to obtain the glow from a solution of copper ore which was supposed to carry platinum I discovered that copper itself, if in sufficient quantity, and when changed to copper oxide, will give the incandescent glow. This fact was theretofore unknown and my discovery thereof forms the subject of an investigation by the Government of the United States of America for the reason that assayers and others have depended on the glow reaction to prove the presence of platinum. A glow was obtained from all the metals herein referred to.

It has been known heretofore that the above metals and oxides will catalyse oxidation reactions but the endeavour has always been to keep the temperature as low as possible, in such processes, and to combine gases so as to produce a useful chemical compound. My purpose is to produce useful heat for industrial and domestic heating, usually at temperatures from 600° C. upward, and an end product, such as CO_2, H_2O, etc., which is of no further use.

It has been proposed to prepare nitrogen and carbonic acid by completely burning a mixture of carbonaceous matter and combustion products such as the exhaust gases (carbon dioxide) for an internal combustion engine in the presence of a catalyst such as copper oxide.

The present invention consists in the process of combustion with the aid of a catalyst for the production of heat in industrial and domestic heating, which comprises using as the catalyst an oxide of at least one of the metals, copper, cobalt or nickel, and wherein the catalyst is preliminary heated and thereafter fuel is burnt with the aid of the heated catalyst in the presence of air and in the absence of carbon dioxide supplied from an external source, and the catalyst becomes incandescent and radiates heat.

The invention also consists in the process of combustion with the aid of a catalyst for the production of heat in industrial and domestic heating, in which heat, preferably as non-luminous flame, and air or oxygen are supplied to the catalytic material, comprising an oxide of at least one of the metals copper, cobalt or nickel, or to said oxides in or on one or more carriers, the carriers being of incombustible material, preferably porous, or of metals which are oxidised upon their surfaces, and thereafter the flame, if any, is extinguished or removed, and fluid fuel and air or oxygen, or air and steam are supplied to the heated oxides, or carriers and oxides, and catalytic combustion is initiated in the absence of carbon dioxide supplied from an external source and a portion of the heat developed is utilised for maintaining the oxides at a temperature sufficient to facilitate catalytic combustion.

Further features of invention will be hereinafter described and defined in the claims.

In order to find a more suitable supporting substance than asbestos I tried many substances and thereby discovered that when certain substances which are relatively difficultly combustible, such, for example, as arc-light carbon, are impregnated with certain solutions, such as copper solutions, by alternate heating to incandescence and soaking immediately with a saturated solution four or five times and finally again heated to incandescence, they will continue to burn, in air, until the carbon therein is all consumed. This they will not do without the presence of such catalyser. This is a new discovery and heretofore unknown. The natural conclusion from the above is that these catalytic substances, in presence of heat, take oxygen from air and pass it over to the combustible element or compound in a purified or concentrated form so that it will activate substances which cannot ordinarily be burned, and will accelerate the rate of combustion of ordinarily combustible elements or compounds.

When catalysers of copper, nickel or cobalt, or mixtures thereof, are precipitated from saturated solution into a porous supporting substance, such for example as diatomaceous earth or granulated firebrick, etc., from two to four times with alternate heating as above described, or when salts of these metals are melted on porous surfaces and heated to incandescence and thereby changed to oxides the surface area of the oxides is vastly greater than when the said oxides are otherwise formed, as by calcining ore concentrates. The degree of catalytic activation is thereby greatly increased. Catalytic combustion may be a form of so-called "flameless" or "surface" combustion. What I call a catalyser, for the purpose of catalytic combustion, may be defined as the more or less finely divided oxides of copper, or nickel, or cobalt, or mixtures thereof. For the purposes of this Specification I also call the combination of such catalysers with their supporting substance a catalyser. In the old process of surface combustion, which will be referred to in more detail below, any refractory substance has been called a catalyser, or catalytic surface. There are important differences in the character of the catalytic action, as between the oxides of said metals on the one hand and ordinary refractory surfaces on the other hand. These will be explained below.

What has been called surface combustion has been known for many years. It is based on the principle that when any more or less refractory substance, such as firebrick, porcelain, etc., is heated to incandescence by means of a gas flame, in presence of air, and the flame then extinguished by momentarily interrupting the flow of the gas, the surface of the refractory will maintain the incandescence without any ordinary flame as long as the gas, mixed with air, impinges on it a sufficiently high velocity. The principal difference between such surface and the said oxides, as catalysers, is that the refractory must first be brought to incandescence by the flame, thereby absorbing a large amount of heat and requiring considerable time; whereas only a relatively low temperature, usually less than 300° C., is necessary to start the reaction in the case of the said oxide catalysers, and this requires much less time. When saturated sulphate solutions are used the sulphur must be thoroughly burned out. When copper nitrate solutions are used the oxides become active at about 290° C. Nickel oxides require more heat and cobalt oxides still more. Nickel oxide surfaces produce a brighter incandescence than copper oxide surfaces at the same pressures but the "incendivity" of copper oxide is less than that of nickel oxide. By the term "incendivity" is meant the ability to effect ignition (see Publications of the Safety in Mines Research Board, volume 1, pages 8 and 9.) These oxides, at certain critical temperatures, become instantaneously incandescent and thereafter greatly accelerate the rate of combustion of the gas, the heat being concentrated at the surface of the oxides and radiated therefrom. The advantages of this low-temperature activation will be more fully explained in connection with a practical application. It will be evident that, because of this low temperature, necessary to initiate the reaction, the catalytic power of the said oxides is much greater than that of ordinary refractory surfaces. Because of this greater power such substances, for example, as arc-light carbon, can be activated by said oxides, as above described.

For the maintenance, without ignition to flame, of relatively low temperatures, namely, nearly up to the ignition temperature of the particular combustible used, it is not necessary to use a high velocity, whereby noise due to the higher pressure is avoided. The intense catalytic action raises the ignition point by inducing or maintaining flameless combustion, by which the "incendivity" of the surface is reduced.

For the maintenance of higher temperatures, from the ignition temperature of the combustible used upward to the highest attainable temperatures, at least such a velocity is required as will give less time of contact of the combustible with the glowing surface for its whole length than the time period of what is known as the "lag on ignition", in order to prevent ignition to flame, or "back firing". The time period of the "lag on ignition" varies, and the degree of incendivity of the surface is dependent: (1) on the temperature of the surface; (2) time of its contact with the combustible; (3) its catalysing power which by inducing flameless combustion reduces the incendivity and raises the temperatures attainable without ignition to flame.

In the old surface combustion process granulated refractory, such as firebrick, has been placed in the fire tubes of steam boilers, and packed around crucibles for melting metals. Although high temperatures of flameless combustion have been attained, when treated as described, the incandescence did not spread throughout the mass of the refractory. For example, W. A. Bone used 3′ × 3″ fire tubes filled with the granulated refractory in which case only that portion of the refractory in the tube near the entrance became incandescent, while the portion farther back in the rear of the tube was warmed by the heat of the portion at the entrance, thus only acting as a baffle to absorb heat. On the other hand, when substances such as diatomaceous earth, which is of a highly porous nature, are impregnated with the said oxides and used in the same way the incandescence readily and quickly spreads throughout the length of a long fire tube. I have obtained this result with city gas at a pressure of only six inches of water, and air at atmospheric pressure, in a five foot by three inch tube. This is because of the relatively low temperature required to initiate the reaction with such oxides as catalysers. It will, therefore, be readily seen that a much higher rate of average evaporation of steam per square foot per hour can be obtained with my catalysers than by the old method. In other words, whereas in the old process a steam evaporation of 35 pounds per square foot per hour was obtained, for the first foot only, of the three feet by three inches fire tube, this was 70 per cent. (seventy) of the total evaporation. On the other hand, with my catalysers a much higher average rate of evaporation per square foot per hour may be obtained for the whole length of the tube. A further advantage of my catalyser is that much less time is required to raise the temperature and increase the rate of evaporation. Due to an even expansion and contraction of the tubes, where my catalysers are used, other advantages are gained. The above advantages apply to heaters for cooking, general heating purposes, raising steam for power, melting and annealing metals, and many other purposes and methods of producing heat. In explosion motors probably a partial catalytic preliminary combustion lessens the violence of detonation and permits higher pressures.

Where liquid fuels are gasified the catalytic oxides may be used in a porous support as described and also injected with the gas if desired. For some purposes a catalyser support, such as diatomaceous earth carrying copper oxides, etc., may be made to absorb the liquid fuel, the earth acting like a lamp wick. This is then lighted with a flame. After the surface becomes incandescent the flame is removed by shutting off air. Air or oxygen, or steam and air, preferably under pressure, is then quickly re-admitted at one or more points along the combustion zone: or heat may be first applied and then a spray of the liquid fuel. The surface will glow with incandescence as long as there is any liquid fuel left in the supporting substance. By supplying a continuous feed or spray of liquid fuel this method may be used for ordinary heating purposes in a suitable apparatus.

These catalysers may be used, in general, in any suitable form of heater, boiler, crucible or muffle furnace, fireplace, cooking stove, heating stove, etc., either as precipitations in porous substances which will burn, or in such as will not burn. In the latter case the combustible element would be a gas or a liquid. The porous supporting substance may be given any suitable shape or size, and applied in a suitable manner such as lumps in fire tubes or crucible furnaces, as bricks, blocks, cylinders, etc., in such manner that the catalytic glowing or incandescent surfaces radiate their heat where it is useful. Molten oxides may be cast into suitable shapes, or formed on one side of copper vessels, etc. When graphite, etc., is used as the support as, for example, in fire tubes, or crucible furnaces, if the gas is in excess the carbon therein will be but little attacked.

In addition to the various combustible substances mentioned I may employ mixtures of air and gas or oil and air and also explosive mixtures thereof.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The process of combustion with the aid of a catalyst for the production of heat in industrial and domestic heating, which comprises using as the catalyst an oxide of at least one of the metals, copper, cobalt or nickel, and wherein the catalyst is preliminarily heated and thereafter fuel is burnt with the aid of the heated catalyst in the presence of air and in the absence of carbon dioxide supplied from an external source, and the catalyst becomes incandescent and radiates heat.

2. The process of combustion with the aid of a catalyst for the production of heat in industrial and domestic heating, in

which heat, preferably as non-luminous flame, and air or oxygen are supplied to the catalytic material, comprising an oxide of at least one of the metals copper, cobalt or nickel; or to said oxides in or on one or more carriers, the carriers being of incombustible material, preferably porous, or of metals which are oxidised upon their surfaces, and thereafter the flame, if any, is extinguished or removed, and fluid fuel and air or oxygen, or air and steam are supplied to the heated oxides, or carriers and oxides, and catalytic combustion is initiated in the absence of carbon dioxide supplied from an external source and a portion of the heat developed is utilised for maintaining the oxides at a temperature sufficient to facilitate catalytic combustion.

3. A process as claimed in Claim 2, in which the time of contact of the fluid fuel and air with the heated catalyst is limited to a time insufficient for the ignition of the fuel to flame at any attainable temperature.

4. A process as claimed in Claim 2 or 3, in which said combustion is initiated by a preliminary heating of the surface of the catalyst to a temperature below incandescence.

5. A process as claimed in any of Claims 1 to 4 wherein air or oxygen, or steam and air, preferably under pressure, is supplied at one or more points along the combustion zone.

6. The improved process of combustion with the aid of a catalyst wherein the catalyst comprises an oxide of one or more of the metals copper, cobalt and nickel substantially as described.

Dated this 10th day of March, 1927.

MARKS & CLERK.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 56A.—125/1/1929.]