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2,942,933

**PROCESS OF OXIDIZING CARBON MONOXIDE
AND HYDROCARBONS IN EXHAUST GASES**

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1 Claim. (Cl. 23—2)

This invention relates to an improved exhaust oxidation system for internal combustion engines whereby the discharge of carbon monoxide and of unburned and partially oxidized products to the atmosphere is prevented or minimized.

When fuels burn in an automotive engine, combustion is relatively incomplete and a considerable portion of the fuel is discharged in the unburned or partially burned condition. Various means have been proposed heretofore for ameliorating this situation, such means generally involving passing the exhaust gases through a bed of oxidation catalyst in the exhaust line. For example, U.S. Patent No. 1,400,959 proposes the use of granulated coke, powdered charcoal and alumina in finely divided form, the catalyst mass being used as a resistance heater by passing electric current from an external source through the mass to raise the same to operating temperatures. U.S. Patent No. 1,903,803 proposes the use of alloy of lead, manganese and copper having an oxidized surface as an oxidation catalyst, while U.S. Patent No. 2,025,140 teaches the use of heavy metal maganites for the same purpose.

Gasoline engines normally run rich; that is, with air-fuel ratios too low for complete combustion of the fuel. Accordingly, if full combustion of the exhaust products is to be effected, oxygen must be supplied to the exhaust either by an air blower (as in U.S. 1,903,803) or by a Venturi eductor as in the present application.

This oxygen or air deficiency varies greatly with different operating conditions. Thus, during normal or cruising conditions, approximately 1 to 4% of the fuel supplied to the engine is discharged unburned. This amount increases to from about 2 to 8% while the engine is idling, or more in traffic (intermittent start and stop conditions) and may be as large as 50% during start-up or under rapid decelerating conditions. While it would be possible to continuously supply the exhaust line with an excess of air large enough to effect complete combustion during periods of normal as well as abnormal (traffic and rapid deceleration) operation, such operation would be inefficient and uneconomical inasmuch as the periods of high air demand are relatively brief and usually occur during only a small proportion of the total operating cycle. Further, the use of unnecessarily large amounts of extraneous air during periods of normal operation would so lower the temperature of any oxidizing catalyst employed as to tend to make the catalyst ineffective.

Accordingly, it is an object of the present invention to provide a means of oxidizing undesired components of exhaust gases which minimizes the use of extraneous air.

It has now been found the desired effect can be secured by employing as oxidation catalyst a polyvalent acid oxide of a metal in groups V through VIII of the periodic table, together with the salts of said oxides, preferably alkali and alkaline earth metal salts thereof.

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The metal in such compounds varies in valence state and the compound thus in oxygen content, depending on whether the compound is subjected to oxidizing or reducing conditions. When subjected to contact with air at elevated temperatures, they take on an elevated valence and (in effect) store oxygen. When subjected to contact with reducing gases such as carbon monoxide or hydrocarbons (in the absence of sufficient extraneous air) such compounds become reduced to lower valence states and thus liberate oxygen which serves to oxidize the reducing gases. The catalyst thus serves as an oxygen reservoir to be drawn on when the supply of added air is insufficient to maintain the catalyst in the more fully oxidized state. This makes it possible to so operate as to supply only an average amount of extraneous air to an internal combustion engine exhaust line, and to depend on the catalyst itself for oxygen during periods of abrupt and brief, peak oxygen demand, the said average extraneous air supply being maintained at such a level that the catalyst becomes reoxidized during normal and steady operation of the engine.

The polyvalent metal-containing catalyst employed in the oxidation chamber should be one of high surface area and which is characterized by good activity even after repeated exposure, over relatively long operating periods, to the high temperatures of exhaust gases. Representative catalysts, which are generally supported on a base material of high surface area such as activated alumina, silica, or the like, are MoO_3 , WO_3 , VO_3 , V_2O_5 , Ta_2O_5 , NaMnO_4 , Na_2MnO_4 , K_2MnO_4 , $\text{Ca}(\text{MnO}_4)_2$, $\text{Ba}(\text{MnO}_4)_2$, Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 , K_2WO_4 , Na_2VO_4 , Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, CaCrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. In general, the oxidation catalyst is present in an amount of from about 2 to 30%, based on the overall weight of the catalyst and its support.

A particularly useful oxidation catalyst was obtained by impregnating an activated alumina of high surface area with potassium dichromate. The pore volume of the support was determined by water displacement. A water solution of potassium dichromate was then prepared of such concentration that the quantity of absorbed solution would result in a finished catalyst containing 14 wt. percent of potassium dichromate. The catalyst was then dried at 250° F. and calcined for four hours at 1,200° F. This catalyst was somewhat active at about 700° F., and is fully active at about 900° F., as heated by the exhaust gases. In the absence of an excess of air over that stoichiometrically required to completely burn the exhaust gas components, the chromium catalyst becomes reduced to the trivalent form and thus releases a substantial amount of oxygen to the combustion process. By thus maintaining a reservoir of oxygen for use during periods of abnormal engine operation, as under decelerating conditions, it is possible to effect full combustion of exhaust components while supplying less excess air to the exhaust stream than would otherwise be required. This feature also characterizes the catalysts enumerated above. Thereafter, as normal engine operation is resumed, with an exhaust stream relatively rich in free oxygen, the catalyst reverts to the $\text{K}_2\text{Cr}_2\text{O}_7$ state, thereby resuming the dual function of an effective oxidation catalyst and an oxygen reservoir. This catalyst was in the form of $\frac{3}{16}$ -inch pellets. However, larger or smaller catalyst particles can be employed, as desired, provided flow of gases through the catalyst body is not unduly restricted.

In carrying out the present invention, extraneous air is, as noted above, introduced into the exhaust manifold by the use of a venturi or other air supplying device at a point upstream from the catalyst chamber which may replace the conventional muffler or supplement the action of the same. The quantity of air so introduced is propor-

tioned to provide the exhaust line with an amount of free oxygen which is at least that stoichiometrically required to burn completely the carbon monoxide and hydrocarbons contained in the exhaust gas under normal (i.e., cruising) conditions of operation. More specifically, good results are obtained when the quantity of air is sufficient to provide an amount of oxygen equal to about 100 to 200% (preferably 125 to 150%) of said stoichiometrical requirement.

The amount of catalyst to be employed for a given engine will vary depending on the size of the engine and upon the length of the desired service period. However, with a 14% $K_2Cr_2O_7$ alumina catalyst of the type described above, for example, it is considered that an amount of from about 10 to 25 pounds thereof will be adequate for the average automobile engine. It is contemplated that the operator will be able to determine whether or not the catalyst is functioning efficiently (as by the use of a temperature indicating device responsive to the exothermic heat generated by an efficient catalyst, for example), and that when the catalyst gives evidence of wearing out, replacement thereof may be made. This may conveniently be accomplished by providing the catalyst in the form of a cartridge which can be removed for inspection and/or replacement at will.

The present invention is illustrated by the following examples.

Example I

Laboratory experiments were conducted to evaluate the 14% potassium dichromate alumina pelleted material as a catalyst for oxidizing hydrocarbons present in an engine exhaust. Mixtures consisting of 1-3% of butane in pure nitrogen and of like amounts of butane in air were passed through the catalyst at various temperatures. The following conclusions were drawn from the results.

(1) At an initial catalyst temperature of 900° F. butane was readily oxidized to carbon dioxide with the formation of only trace amounts of olefins and other byproducts.

(2) At an initial temperature of 500° F. the butane was oxidized, but at a rate too slow to be practical. A much more promising rate was achieved at 700° F.

(3) One mol of dichromate makes available 1.5 mols of oxygen as it is reduced to the Cr_2O_3 state. When a stream of butane in nitrogen was oxidized in the absence of extraneous air, more than 90% of the paraffin was converted to CO_2 until about half of the dichromate was reduced. The rate of conversion then fell off rapidly, though the butane continued to be oxidized until the dichromate was substantially all reduced.

(4) Addition of 1.5 times the stoichiometric amount

of oxygen caused the butane to be completely oxidized during a period in which sufficient butane was passed over the catalyst to reduce 25 times the amount of dichromate that was present. No evidence of depletion in catalyst activity was observed, showing that the dichromate on alumina was acting as a true catalyst.

Example II

A chamber containing about 12 pounds of the same potassium dichromate catalyst as employed in Example I, was designed to replace the muffler of a 1954 Chevrolet 6. Air was introduced into the exhaust stream by means of a venturi upstream from the muffler, the air so introduced being about 15% by volume of the resulting exhaust stream. It was found that the catalyst was highly effective in oxidizing the hydrocarbons present in the exhaust under varying operating conditions. Thus, at a catalyst temperature of about 1,000° F., nearly quantitative combustion of the hydrocarbons was achieved under idling conditions. About two-thirds of the hydrocarbons were burned at 30 miles per hour, and a further reduction in noncombusted gases could have been obtained by increasing the volume of catalyst. The catalyst chamber did not produce excessive pressure drop in the exhaust system even under full-throttle conditions. The products of the combustion of tetraethyl lead in the gasoline did not poison the catalyst. The chamber functioned without being supplied with external heat. However, in normal city driving at low speed it might be desirable to initiate the reaction with external heat, which could be cut off after the chamber began to function. Since the reaction is exothermic, the catalytic combustion would then be self-sustaining.

We claim:

The process of effecting substantially complete combustion of automotive exhaust gases, which comprises passing said gases, along with added air in an amount of from about 100 to 200% of that stoichiometrically required to burn completely the carbon monoxide and hydrocarbons contained in the exhaust gases under normal conditions of engine operation, through an oxidation catalyst comprising from 2 to 30% of potassium dichromate disposed on an activated alumina support.

References Cited in the file of this patent

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