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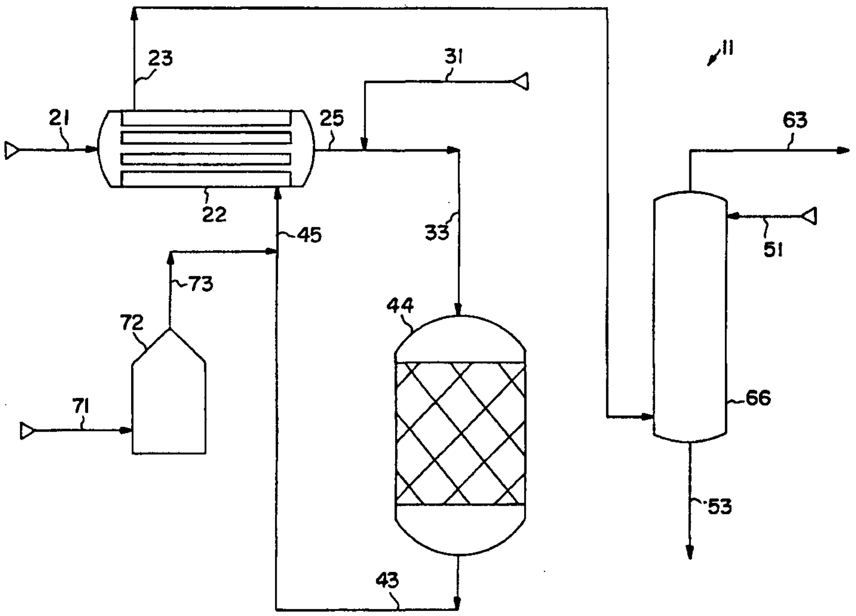

(57) Abstract

An integrated process of vent gas treatment for abatement of carbon monoxide and volatile organic compound emissions from a chemical process plant is provided, and includes provisions for catalytic oxidation of organic pollutants with dioxygen in a vent gas stream over a solid oxidation catalyst (44), means for supplying an amount of combustible fluid (31) into the vent gas stream upstream of the oxidation to facilitate catalytic oxidation of the organic pollutants; and means for controlling the amount of combustible fluid being supplied by the supplying means, the controlling means being arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures in accordance with the present invention.

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ATALYTIC VENT GAS TREATMENT SYSTEM FOR ABATEMENT OF VOLATILE CHEMICAL EMISSIONS

Technical Field

This invention relates to catalytic vent gas treatment systems for abatement of volatile chemical emissions. More particularly, the present invention relates to apparatus and methods for abatement of carbon monoxide and volatile organic compound emissions from industrial processes having a vent gas stream containing potential pollutants.

The instant invention provides vent gas treatments which include; (A) dispersing into a vent gas stream a controlled amount of a preselected combustible fluid, (B) simultaneously oxidizing the combustible fluid and destroying a substantial fraction of the hazardous volatile organic compounds by oxidation over an oxidation catalyst at elevated temperatures, and (C) controlling the amount of combustible fluid being delivered to the vent gas stream so as to provide sufficient reactants for the catalytic oxidation to maintain a suitable range of reaction temperatures.

Several aspects of this invention relate to processes for commercial manufacture of organic acids, particularly dibasic aromatic acids formed from a corresponding methyl substituted aromatic compound by liquid-phase oxidation of the methyl groups by contact with source of dioxygen, such as compressed air, in the presence of an oxidation catalyst system containing one or more compounds derived from a halogen. Integrated treatment systems according to this invention are, advantageously, used for abatement of carbon monoxide and volatile organic compound emissions from liquid-phase oxidation processes of forming aromatic acids.

Processes in accordance with this invention achieve, typically, destruction efficiencies for carbon monoxide in a range upward from about 90 percent to about 95 percent and higher, destruction efficiencies for hydrocarbons in a range upward from about 80 percent to about 90 percent or greater. Processes using selected oxidation catalysts in accordance with this invention may, advantageously, achieve destruction efficiencies for alkyl halide compounds in a range upward from about 50 percent to about 85 percent or more.

Background of the Invention

Both thermal and catalytic incineration is widely known and used for destruction of hazardous volatile organic compounds found in waste air and other gas streams which result from a variety of industrial processes. These streams result from processes for manufacture of organic chemicals and polymers, and from operations in which volatile organic solvents are used for cleaning and degreasing purposes in metal processing, machining and finishing. While catalytic incineration is able to operate at significantly lower temperatures and with considerably lower residence times than the thermal incineration alternative, additional equipment including a furnace and/or other heat exchange equipment have, typically, been required to provide a suitably elevated operating temperature to obtain catalytic activity for destruction of hazardous volatile organic compounds from a variety of industrial processes.

In any commercially viable application of catalytic incineration, special care is required in selection of an oxidation catalyst system appropriate to the volatile organic compounds which it is desired to destroy, and to avoid exposure of the selected catalyst to compounds which destroy its catalytic activity. Many of the gas streams which must be treated contain significant amounts of a halogen and/or halogenated compounds. However, some precious metal catalysts used in conventional catalytic incineration are severely inhibited in their performance by the halogen atoms from the destruction of these compounds, and this desirable process cannot generally be used with such catalysts for these gas streams.

Recent and continuing interest in reduction of atmospheric pollution from internal combustion engines used in automotive and other vehicular applications is shown by numerous disclosures of apparatus for such intermittent operation. It is typically, stated that a reduction of atmospheric pollution and/or that some regulatory standard could be met using the disclosed apparatus. Achievement of significant improvement, however, may depend upon combination of any particular apparatus with modified engine designs and special fuels. Fuel quality improvements included, generally, both removal from the fuel composition of compounds which are known precursors of particular pollutants and blending with additional compounds which may change the composition of exhaust gases.

Recently issued U. S. Patent Number 5,193,340 in the name of Tetsuya Kamihara and assigned to Nissan Motor Co. Ltd., is a representative of exhaust gas systems for internal combustion engine application. Most diesel engines are now equipped with a trap filter dispose in an exhaust passageway for trapping particulates and the like which are discharged from a diesel engine. When the back pressure of the engine increases due to the accumulation of the particulates trapped by the trap filter, the particulates are periodically burned to regenerate the trap filter. In the Kamihara apparatus the trap filter contains an oxidation catalyst for assisting burning of the particulates collected in the filter prior to regeneration. An injector valve is provided to inject diesel fuel into the exhaust passageway upstream of the trap filter, so that the trap filter is supplied with diesel fuel. The diesel fuel is burned in the tap filter under the action of the oxidation catalyst thereby burning the particulates so as to achieve a regeneration operation for the trap filter. When in operation, the amount of diesel fuel injected is controlled to increase as an intake air amount supplied to the engine increases and to decrease as an exhaust gas temperature increases, to limit or avoid thermal damage to the trap filter. When the particulates are periodically burned to regenerate the trap filter, the back pressure of the engine due to the accumulation of the particulates trapped by the trap filter is decreased thereby preventing the pack pressure from affecting engine performance. Undisclosed amounts of increased gaseous pollutants are exhausting to the atmosphere from the system during regeneration operation due to the additional diesel fuel burned.

Additional methods for filtering combustible particles from exhaust gases and rejuvenating the filter bed and its catalyst section are, for example, described in U.S. Patent No. 4,322,287, U.S. Patent No. 4,359,862 and U.S. Patent No. 4,372,111 in the names of Kashmir S. Kirk and Martin Alperstein, and U.S. Patent No. 4,359,863 in the names of Kashmir S. Kirk and Robert B. Burns, all assigned to Texaco Inc.

An earlier example of catalytic incineration equipment in which a gas-permeable bed of solids adapted to exchange heat with a gas stream is alternately heated with hot effluent from a catalytic oxidation bed and cooled with gas flowing into the bed by periodically reversing the direction of gas flow through the beds is described in U.S. Patent No. 2,946,651 in the name of Eugene J. Houdry and assigned to Oxy-Catalyst, Inc. In operation, the patent states that sufficient diesel oil was injected into the heated gas stream and vaporized and then catalytically oxidized on the catalytic bed being used to heat the bed of gas-permeable solids. The catalyst employed was in the form of pellets of activated alumina impregnated with 5 percent of copper and chromium oxides and 0.1 inch in size. The heat exchange bed was the same size pellets composed of a dense fused alumina (Corhart).

Additional methods using preheating and or reversing flow for catalytic cleaning of exhaust gases are, for example, described in U.S. Patent No. 4,059,676 in the names of Kang Yang and James D. Reedy, and assigned to Continental Oil Company; U.S. Patent No. 4,877,592 in the names of Jury S. Matros, Viktor A. Chumachenko, Ljudmila J. Zudilina, Alexandr S. Noskov and Evgeny S. Bugdan, and assigned to Institut Kataliza Sibirskogo Otdelenia Akademii

Nauk SSSR; Spetsialnoe Konstruktorsko-Technologicheskoe Bjuro Katalizatorov S Optnym Zavodim; and in U.S. Patent No. 4,966,611 in the names of John C Schumacher, Joesph C. McMenamin, Lawrence B. Anderson, Harold R. Cowles and Stephen M. Lord, and assigned to Custom Engineered Materials Inc.

Regardless of the apparatus and methods employed, each commercial use depends, to be successful, upon selection of an oxidation catalyst appropriate to the volatile compounds which it is desired to destroy and the active lifetime of the catalyst in that system. Useful catalyst life is often limited due to exposure of oxidation catalysts to compounds which destroy their catalytic activity. Historically, the presence significant amounts of a halogen and/or organic and inorganic halogenated compounds in many of waste gas streams which must be treated has prevented the use of catalytic oxidation as a control technology for this application. It is believed the presence of halogen and/or compounds derived from halogen, whether or not such compound are destroyed in the process, deteriorate and temporarily poison the performance of some precious metal catalyst.

Catalysts containing a nobel metal (platinum), optionally in combination with other metals, for burning combustibles are described in U.S. Patent No. 3,378,334 in the name of Herman S. Bioch and assigned to Universal Oil Products Company. Hydrated metal oxide catalysts have also been described. For example, U.S. Patent No. 4,059,677 in the names of Edward J. Sare and Jerome M Lavanish, and assigned to PPG Industries, Inc., teaches that a waste containing C_2 - C_4 halogenated hydrocarbons, particularly unsaturated chlorinated hydrocarbons such as vinyl chloride, are incinerated in the presence of combination the hydrated oxides of manganese and cobalt. A supported catalyst system containing a Group VIII metal (platinum) is disclosed in U.S. Patent No. 5,145,826 in the names of Eugene H. Hirschberg and George A. Huff, Jr., and assigned to Amoco Corporation. The disclosures of U.S. Patent Nos. 3,378,334, 4,059,677 and 5,145,826 are specifically incorporated herein in their entirety by reference.

U.S. Patent No. 5,292,704 in the name of George R. Lester and assigned to Allied-Signal Inc.., teaches that a waste containing C_1 halogenated compounds that do not have any carbon-hydrogen bonds are incinerated to carbon dioxide and halo acids (HCl, HBr, etc.) in the presence of specific combinations of a noble metal (platinum, palladium and rhodium), active catalytic components of titania, vanadium oxide, tungsten oxide, and optionally an effective amount of water. The disclosure of U.S. Patent No. 5,292,704 is specifically incorporated herein in its entirety by reference. Halo acids are, however, very corrosive pollutants.

It is therefore a general object of the present invention to provide improved apparatus and methods which overcome the aforesaid problems of prior art methods for abatement of carbon monoxide and volatile organic compound emissions from a chemical process having a waste gas or vent gas stream containing a mixture of potential pollutants.

More particularly, it is an object of the present invention to provide integrated catalytic vent gas treatment systems for abatement of hazardous emissions from industrial processes using volatile chemicals.

It is another object of the present invention to provide integrated catalytic vent gas treatment systems that reduces air pollution by achieving reduced vent gas particulate levels emitted to the atmosphere.

It is another object of the present invention to provide integrated catalytic vent gas treatment systems that achieves reduced carbon monoxide and levels of potential pollutants at lower operating temperatures.

It is another object of the present invention to provide integrated catalytic vent gas treatment systems that achieves increased fuel efficiency and reduced fuel requirements while controlling carbon monoxide and levels of potential pollutants.

It is yet another object of the present invention to provide integrated catalytic vent gas treatment systems that extends incinerator equipment life, reduces maintenance costs, and reduces the frequency and duration of facility downtime.

It is yet another object of the present invention to provide integrated catalytic vent gas treatment systems with reduced energy costs.

While the above objects can be attained by integrated catalytic vent gas treatment systems according to this invention, other objects and advantages of the invention will become apparent upon reading the following detailed description and appended claims.

Summary Of The Invention

Economical treatment systems are disclosed for abatement of carbon monoxide and volatile organic compound emissions from chemical processes having a vent gas stream containing potential pollutants and excess dioxygen. Processes according to this invention include, broadly, (A) dispersing into the vent gas stream a controlled amount of a preselected combustible fluid, (B) simultaneously oxidizing the combustible fluid and destroying a substantial fraction of the organic pollutants by oxidation over an oxidation catalyst at elevated temperatures, and (C) controlling the amount of combustible fluid being delivered to the vent gas stream so as to provide sufficient reactants for the catalytic oxidation to maintain a suitable range of reaction temperatures.

Selection of combustible fluid is critical in order that its oxidation provide a substantial amount of the heat that is required to control operating conditions over the oxidation catalyst without deleterious effect on catalyst activity. Advantageously, compounds in the combustible fluid should be in the vapor state at operating conditions. Suitable combustible fluids comprise carbon monoxide, hydrogen, hydrocarbon compounds, and organic compounds containing at least one oxygen atom per molecule. Generally, organic compounds useful as combustible fluids according to this invention consists of compounds, such as alkanes, alkenes, alcohols, ethers, aldehydes (alkanals), ketones (alkanones), organic acids and mixtures thereof, which have normal boiling points in a temperature range downward from about 200° C to about -165° C, preferably in a temperature range downward from about 160° C to about -50° C and more preferably in a temperature range downward from about 130° C to about 30° C. Preselected combustible fluid comprises a member of the group consisting of carbon monoxide, hydrogen, C_1 to C_5 hydrocarbon compounds, C_1 to C_5 organic compounds containing at least one oxygen atom per molecule and mixtures thereof, preferably at least one member of the group consisting of carbon monoxide, dihydrogen (H_2), methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and 2-methyl-2-propanol.

Examples of useful combustible fluids include propane, butane, pentane, ethene (ethylene), propene (propylene), 1-butene (α-butylene), 2-butene (β-butylene), methylpropene (isobutylene), 1-pentene (α-amylene), 2-Pentene, 2-methyl-1-butene, 2-methyl-2-butene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol (isobutyl alcohol), 2-methyl-2-propanol (*tert*-butyl alcohol), methoxymethane (dimethyl ether), methoxyethane (methyl ethyl ether), ethoxyethane (diethyl ether), 1-methoxypropane (methyl *n*-propyl ether), 2-methoxypropane (methyl isopropyl ether), 1-methoxybutane (methyl *n*-butyl ether), methanal (formaldehyde), ethanal (acetaldehyde), propanal (propionaldehyde), butanal (n-butyraldehyde), methylpropanal (isobutyraldehyde), pentanal (*n*-valeraldehyde), dimethylpropanal (pivaldehyde), propanone (acetone), butanone (methyl ethyl ketone), 3-pentanone (diethyl ketone), 2-pentanone (methyl *n*-propyl ketone), methane, ethane, and mixtures thereof.

In broad aspect, the invention is a vent gas treatment system for abatement of carbon monoxide, volatile hydrocarbon and other volatile compound emissions from a chemical process plant having a vent gas stream containing potential pollutants and excess dioxygen. More particularly, a system includes; an oxidation vessel, containing a solid oxidation catalyst, disposed in the vent gas stream; means for determining temperature of the vent gas stream upstream of the oxidation catalyst; means for supplying an amount of combustible fluid into the vent gas upstream of the oxidation pressure vessel to facilitate catalytic oxidation of the organic pollutants; means for determining temperature of the vent gas downstream of the oxidation catalyst; and means for controlling the amount of combustible fluid being delivered by the supplying means, the controlling means being arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures.

Vent gas treatment systems according to the instant invention may, advantageously, include a gas to gas heat exchanger, disposed in both the oxidation effluent stream from the oxidation vessel and the untreated vent gas stream to transfer heat therebetween. Optionally a gas scrubber may be disposed in the oxidation effluent down stream of the gas to gas heat exchanger.

In another aspect, the invention is a process of vent gas treatment for abatement of carbon monoxide, volatile hydrocarbon and alkyl halide compound emissions from a chemical process plant having a vent gas stream containing organic pollutants and excess dioxygen. This process includes: (A) Dispersing into the vent gas stream a controlled amount of combustible fluid where temperatures of the vent gas stream are in a range of temperature upward from about 25° C, typically in a range of temperature from about 30° C to about 600° C; (B) Oxidizing the combustible fluid and destroying a substantial fraction of the organic pollutants by oxidation over a selected solid oxidation catalyst at temperatures in a range upward from about 150° C, typically in a range from about 200° C to about 600° C; and (C) Controlling the amount of combustible fluid being delivered to the vent gas stream so as to provide sufficient reactants for the catalytic oxidation to maintain a suitable range of reaction temperatures. One class of suitable combustible fluids is, preferably, selected from the group consisting of hydrogen and organic compounds containing at least one oxygen atom per molecule, which organic compounds have a normal boiling point in a temperature range downward from about 200° C to about -165° C, preferably in a temperature range downward from about 160° C to about -50° C and more preferably in a temperature range downward from about 130° C to about 30° C.

Several aspects of this invention relate to catalytic oxidation processes for commercial manufacture of organic acids and/or their anhydrides, particularly dibasic aromatic acids such as isophthalic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid, or anhydride such as trimellitic anhydride and the like. One or more compound derived from a halogen is, typically, a critical component of the oxidation catalyst system used for commercial manufacture of dibasic aromatic acids. Processes, for example, in which the vent gas stream comprises an effluent containing nitrogen, excess dioxygen, volatile hydrocarbon compounds and other organic compounds, such as volatile alkyl halide compounds, from a liquid-phase oxidation process of forming an aromatic acid from a corresponding methyl substituted aromatic compound by contact with source of dioxygen, such as compressed air, in the presence of an oxidation catalyst system at elevated pressures and temperatures. Integrated treatment systems according to this invention are, advantageously, used for abatement of carbon monoxide and volatile organic compound emissions from liquid-phase oxidation process of forming aromatic acids, such as isophthalic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid and other dibasic acids.

A more detailed explanation is provided in the following description and appended claims taken in conjunction with the accompanying figure.

Brief Description Of The Drawing

The appended claims set forth those novel features which characterize the present invention. The present invention itself, as well as advantages thereof, may best be understood, however, by reference to the following brief description of preferred embodiments taken in conjunction with the annexed drawing, in which:

FIG. 1 is a simplified diagrammatic representation of a portion of an integrated process of vent gas treatment for abatement of carbon monoxide and volatile organic compound emissions from a chemical process plant, and includes provisions for catalytic oxidation of organic pollutants with dioxygen in a vent gas stream over a solid oxidation catalyst, means for supplying an amount of combustible fluid into the vent gas stream upstream of the oxidation pressure vessel to facilitate catalytic oxidation of the organic pollutants; and means for controlling the amount of combustible fluid being supplied by the supplying means, the controlling means being arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures in accordance with the present invention.

Brief Description Of The Invention

Catalytic vent gas treatment systems for abatement of volatile chemical emissions according to this invention are, suitably, used for destruction of volatile organic compounds found in waste air and other gas streams involved with a wide variety of industrial processes. Such streams result, for example, from processes for manufacture of organic chemicals and polymers, fabric coating, food processing, rubber fabrication operations, and from operations in which volatile organic solvents are used for coating, cleaning and/or degreasing purposes in metal processing, machining and finishing.

Vent gas streams suitable for treatment in the catalytic process of the present invention can comprise most materials that are combustible in the presence of oxygen at temperatures within the operating range of the catalytic device. These materials are generally, but not limited to, carbon monoxide, hydrogen, hydrocarbon compounds, and organic compounds containing other atoms such as oxygen, nitrogen, halogens and the like . Generally, potential pollutants include volatile compounds, such as alkanes, alkenes, alcohols, ethers, aldehydes (alkanals), ketones (alkanones), organic acids and mixtures thereof, which form vapors found in a vent gas stream.

For safe operation the amount of organic compounds in the waste air or vent gas streams should, generally, be substantially below the lower explosive limit (LEL) at operating conditions, preferably in a range downward from about 50 percent of the LEL, and more preferably below about 25 percent of the LEL. The composition of the gas streams is, typically, monitored by on-line analysis equipment for safe operation, while controlling the amount of combustible fluid being delivered to the vent gas stream so as to provide sufficient reactants for the catalytic oxidation to maintain a suitable range of reaction temperatures.

The range of total reactor pressure useful in this invention runs between sub-atmospheric and about 1000 psig, preferably between sub atmospheric and about 600 psig, more preferably between atmospheric and about 300 psig, and most preferably from about 10 psig to about 200 psig.

Vent gas treatments in accordance with the present invention, include contacting the waste gas stream with a catalyst in the presence of excess oxygen at suitable temperatures which are, typically, in a range downward from about 600° C. Operations of the present invention are, advantageously, carried out at inlet temperatures to the oxidation catalyst in a range downward from about 550° C to about 50° C, depending upon the composition of the waste gas stream and the nature of a particular catalyst system. Catalysts do not alter the reaction product composition at equilibrium, but can accelerate the reactants toward their equilibrium at lower energy levels (lower operating temperatures). While a true catalyst is not consumed in the reaction, catalysts may be poisoned or deactivated by the presence of particular compounds in the waste gas stream or severe operating conditions.

The range of useful volume hour space velocities run between about 100 hr^{-1} and about 200,000 hr^{-1}, preferably between about 1000 hr^{-1} and about 50,000 hr^{-1}, based upon volume of catalyst.

In accordance with the present invention, the oxidation catalyst comprises a combustion promoting metal deposed on a catalyst support. Base metal catalysts can be used for treatment of waste streams containing CO and/or organic compounds which have a high relative destructibility, such as alcohols, cellosolves, aldehydes and the like. In general, the higher the molecular weight of a particular class of organic compound, the higher its relative destructibility. Nobel metal catalysts are, advantageously, used for treatment of waste streams containing organic compounds which have lower relative destructibility, such as aromatics, ketones, acetates, alkanes, halogenated hydrocarbons and the like.

In the instant invention the catalyst can be used in any convenient configuration, shape or size which exposes the oxidation promoting components of the catalyst to the gas stream to be treated. For example, catalyst can be in the form of pills, pellets, granules, rings, spheres, etc. Particulate forms are especially desirable where large volumes of catalysts are needed, an for use in circumstances in which periodic replacement of the catalyst may be desired. In circumstances in which less mass is desirable or in which movement or agitation of particles of catalyst may result in attrition, dusting and resulting loss of dispersed metal or undue increase in pressure drop across the particles, a monolithic form is preferred. In accordance with the present invention, catalysts are, typically, used in a pelleted or monolithic form.

The support for the oxidation catalyst can be less catalytically active or even inert to the oxidation reaction. Desirably, the support is porous and has a surface area, including the area of the pores on the surface, of at least from about 25 m^2 /gm to about 250 m^2/gm, preferably from about 50 m^2/gm to about 200 m^2/gm, and more preferably from about 80 m^2/gm to about 150 m^2/gm for best results. Suitable supports for use in the present invention include mullite, spinel, sand, silica, alumina, silica alumina, titania, zirconia, alpha alumina, gamma alumina, delta alumina, and eta alumina. Supports comprising alpha alumina, gamma alumina, silica, or silica alumina are preferred. Supports comprising alpha alumina or gamma alumina are more preferred.

The support component of the oxidation catalyst may be pure or a composite of materials. Composite supports are advantageous where there is a desire to add particular chemical or physical characteristics to the catalyst. For example, the oxidation catalyst can comprise a substrate and a substrate coating in order to attain the particular benefits of both, substrate materials having high attrition resistance and substrate coating materials having high surface area. The substrate and substrate coating can be combined through conventional impregnation techniques. Suitable materials for use as a composite substrate for the oxidation catalyst are mullite, spinel, alpha alumina, and sand. Alpha alumina is the preferred composite substrate. Suitable materials for use as a composite substrate coating are silica, alumina, titania, silica alumina, zirconia, alpha alumina, gamma alumina, delta alumina, and eta alumina. Composite substrate coatings comprising silica, titania, silica alumina, and gamma alumina are preferred. Composite substrates comprising gamma alumina are more preferred.

The combustion promoting metal of the process of the present invention can be the types used or generally known in the art to promote the oxidation of carbon monoxide to carbon dioxide in the presence of molecular oxygen. The metal can be in a combined form, such as an oxide, rather than being in the elemental state. The combustion promoting metal can comprise two or more catalytically-active metals either physically or chemically combined. Suitable combustion promoting metals for use in the process of the present invention are the transition group elements of the Periodic Table (IUPAC), preferably the Group VIII metals, more preferably the precious metals, and more preferably yet, platinum and palladium. Platinum is preferred by reason of its ability to sustain high activity for oxidation of carbon monoxide.

The percentage of combustion promoting metal to add to the oxidation catalyst used in the present invention is a function of catalyst cost and process effectiveness. The preferred concentration of promoter metal is that which achieves process objectives at minimum catalyst cost. Generally, the combustion promoting metal is a costly component of the oxidation catalyst. Higher metal concentrations and lower volume usage reduces the support and oxidation catalyst costs. Suitable metal concentrations on the combustion promoter catalyst of the present invention can range by weight from about 0.1 ppm to about 15,000 ppm, preferably from about 0.5 ppm to about 10,000 ppm, and more preferably from about 1 ppm to about 8,000 ppm for best results.

A platinum group component can be incorporated in the support in any suitable manner , such as by coprecipitation or cogellation with the support, ion-exchange, or by impregnation. Preferably, the platinum group component is substantially uniformly disposed on the support. One preferred method for adding the platinum group component to the support involves the utilization of a water soluble compound of the platinum group component to impregnate the support prior to calcination. For example, platinum may be added to the support by commingling the uncalcined support with an aqueous solution of chloroplatinic acid. Other water soluble compounds of platinum may be employed as impregnation solutions, including for example, ammonium chloroplatinate and platinum chloride.

The oxidation catalyst used in the present invention should have the proper physical characteristics for use in fixed bed oxidation. The most important physical characteristics in the practice of the present process are pressure drop across the catalyst and resistance to attrition.

Several particularly useful waste gas oxidation catalysts have been described. For example, U.S. Patent No. 3,378,334, the disclosure of which is specifically incorporated herein in its entirety by reference, describes a fixed bed of spherical catalyst particles containing up to about 5 percent of a catalytically active metal such as platinum, palladium, iridium, ruthenium, rhodium, various mixtures including platinum-iron, platinum-cobalt, platinum-nickel, palladium-iron, palladium-cobalt, palladium-nickel, platinum-palladium, palladium-copper-cobalt, platinum-copper-lithium-cobalt, platinum-cobalt-copper, copper-cobalt-nickel-platinum, platinum-palladium-cobalt, manganese-platinum, platinum-cobalt-manganese, lithium-platinum-cobalt, copper-cobalt-lithium, etc. These oxidation catalysts are generally constituted in a manner similar to other hydrocarbon conversion catalysts in that they comprise a high surface area refractory inorganic oxide base or support such as alumina, alumina-silica, alumina-zirconia, etc. upon which are deposited by precipitation or impregnation techniques, one or more activating components, i.e., catalytically active metals or metal oxides. Particularly desirable activating component for burning combustible gases are the metals of the platinum family, especially platinum and palladium; these show excellent conversion activity for carbon monoxide, hydrocarbons, and oxygenated hydrocarbons over prolonged periods of time.

Suitable catalysts containing ruthenium, ruthenium plus platinum and platinum dispersed on a non-oxidizing support are described respectively in U.S. Patent Nos. 4,059,675, 4,059,676 and 4,059,683, the disclosures of which are specifically incorporated herein in their entirety by reference. The first patent teaches use of 0.01 to 1.0 weight percent ruthenium on a non-oxidizing support for decomposing chlorinated hydrocarbon compounds containing up to 4 carbon atoms and containing at least as many hydrogen atoms as chlorine atoms at temperatures of at least about 350° C. The second patent teaches use of a bimetallic catalyst wherein both finely divided metallic ruthenium and a noble metal, i.e. 1 to 20 parts of finely divided metallic platinum per part of ruthenium, are supported on a non-oxidizing support for decomposing chlorinated hydrocarbon compounds containing up to 4 carbon atoms and containing at least as many hydrogen atoms as chlorine atoms at temperatures of at least about 350° C. Chlorinated compounds which are decomposed include vinyl chloride and mixtures of C_1 chlorinated compounds and C_2 chlorinated compounds containing vinyl chloride having a total number of hydrogen atoms in the mixture at least equal to the total number of chlorine atoms. Oxidation products CO_2, H_2O, HCl, and Cl_2 are produced using these catalysts.

Suitable catalysts containing (a) iron dispersed on an alumina support and a rare earth metal, particularly oxides of iron and praseodymium, and (b) an intermediate oxide of tungsten in which the average valence state of the tungsten radical is greater than 4 and less than 6, are described in U.S. Patent No. 4,610,975, the disclosure of which is specifically incorporated herein in its entirety by reference.

Catalysts containing palladium and/or platinum and at least three promoter components carried on a porous support are described in U.S. Patent No. 4,857,499, the disclosure of which is specifically incorporated herein in its entirety by reference. The first promoter component includes one of the rare earth elements such as lanthanum, cerium, praseodymium and neodymium, alkaline earth metals such as barium, strontium and calcium, and oxides thereof, the second promoter component includes magnesium, silicon and oxides thereof, and the third promoter component includes one of the heavy metals such as nickel, zirconium, cobalt, iron and manganese and oxides thereof.

More recently, particularly useful catalysts containing titania and optionally tungsten oxide, vanadium oxide, tin oxide and the noble metals platinum, palladium, and rhodium are described in U.S. Patent No. 5,176,897, the disclosure of which is specifically incorporated herein in its entirety by reference, for use with an effective amount of water to convert halogen containing organic compounds to carbon dioxide and the corresponding halo acid.

The following examples will serve to illustrate certain specific embodiments of the herein disclosed invention. These examples should not, however, be construed as limiting the scope of the novel invention, as there are many variations which may be made thereon without departing from the spirit of the disclosed invention, as those of skill in the art will recognize.

Examples Of The Invention

General

In the following examples, simultaneous oxidation of combustible fluids and destruction of substantial fractions of potentially hazardous volatile organic compounds by oxidation over an oxidation catalyst at elevated temperatures were carried out using a small cylindrical reactor (3/4 inch ID, 6 inch L) adapted to contain a supported catalyst bed. External surfaces were heated via electric heaters. Internal surfaces of the reactor were made of materials which exhibited no catalytic activity under various operating conditions used in these examples. Thermocouples were located throughout the apparatus, particularly in the reactor just above and below the catalyst bed.

Combustible fluid and simulated vent gas were continuously metered and passed through a static mixer upstream of the reactor. Temperatures of gaseous mixtures entering the reactor were, typically, about 200° C. Concentrations of organic compounds in reactor feed and effluent gases were determined by gas chromatography using flame ionization detection. Concentrations of carbon monoxide and carbon dioxide were measured using infrared analyzers. Oxygen concentrations were measured with an electrochemical analyzer. Unless otherwise noted, gas compositions are in percent by volume and parts per million by volume (ppmv).

Example 1

In this example, a series of vent gas treatments was carried out according to this invention using methanol as the combustible fluid with a precious metal volatile organic compound destruction catalyst in the form of, or supported on, ceramic monolith.

The gaseous mixtures entering the reactor had compositions of about 2 percent to about 6 percent oxygen, about 0.1 percent to about 0.5 percent carbon monoxide, about 0.5 percent to about 3.0 percent carbon dioxide, about 0.2 percent to about 2.0 percent water, from about 1 ppmv to about 1,000 ppmv each of methyl acetate, methyl bromide, methyl formate, benzene, toluene, *p*-xylene and acetic acid, from about 3,000 ppmv to about 14,000 ppmv methanol and a balance of nitrogen.

At reactor temperatures in a range from about 415° C to about 510° C, reactor pressure of about 160 psig to about 170 psig, and space velocity of about 10,000 hr^{-1} (gas flow rate at standard conditions/catalyst volume), conversions of carbon monoxide, methyl acetate, methyl bromide, methyl formate, benzene, toluene, *p*-xylene and acetic acid were in a range upward from about 97 percent. At reactor temperatures in a range from about 310° C to about 510° C and space velocity of about 10,000 hr^{-1} conversions of methanol were in a range upward from about 99 percent. Analysis of reactor effluent for combustion produces found carbon dioxide, water elemental bromine (Br_2) and hydrogen bromide (HBr). Intermediate oxidation compounds, which could be detected at concentrations above about 1 ppmv, were not detected. Throughout these runs, no deleterious effect on activity of the catalyst was observed.

Comparative Example A

In this comparative example, a series of runs was carried out as in Example 1, but without catalyst and at very low methanol concentrations in a range from about 30 ppmv to about 60 ppmv based on total reactor feed gas. Under operating conditions used in Example 1, there was no significant oxidation of either the organic compounds or the carbon monoxide in reactor feed gas, even at reactor temperatures up to about 550° C, reactor pressure of about 140 psig to about 160 psig,.

Comparative Example B

In this comparative example, a series of runs was carried out as in Example 1, but without addition of any combustible fluid addition to the reactor feed gas and at very low methanol concentrations in a range from about 30 ppmv to about 35 ppmv based on total reactor feed gas. Temperature of the catalyst bed was controlled by heating with the external electric heaters.

The gaseous mixtures entering the reactor had compositions of about 2 percent to about 6 percent oxygen, about 0.1 percent to about 0.5 percent carbon monoxide, about 0.5 percent to about 3.0 percent carbon dioxide, about 0.2 percent to about 2.0 percent water, from about 1 ppmv to about 1,000 ppmv each of methyl acetate, methyl bromide, methyl formate, benzene, toluene, *p*-xylene and acetic acid, and a balance of nitrogen.

At reactor pressures in a range from about 140 psig to about 150 psig and reactor temperatures in a range upward from about 438° C and space velocity of about 10,600 hr^{-1}, conversions of carbon monoxide, methyl acetate, methyl bromide, methyl formate, benzene, toluene, *p*-xylene and acetic acid were in a range upward from about 95 percent. At reactor temperatures in a range upward from about 494° C conversions were in a range upward from about 98 percent.

Comparative Example C

In this comparative example a series of vent gas treatments was carried out as in Example 1, but using hexane as the combustible fluid with a non-nobel metal volatile organic compound destruction catalyst in granular form.

The gaseous mixtures entering the reactor had compositions of about 5.8 percent oxygen, 2.0 percent water, from about 1 ppmv to about 1,000 ppmv each of methyl bromide and methanol, from about 4,000 ppmv to about 5,000 ppmv hexane and a balance of nitrogen.

At reactor temperatures in a range from about 415° C to about 510° C, reactor pressure of about 110 psig to about 130 psig, and space velocity of about 10,000 hr^{-1} (gas flow rate at standard conditions/catalyst volume), conversions of methyl bromide, methanol and hexane were, respectively, about 91 percent, 92 percent and 99.8 percent as determined by decreases in their concentration across the reactor. Analysis of reactor effluent for combustion produces found carbon dioxide, carbon monoxide, water elemental bromine (Br_2) and hydrogen bromide (HBr). However, about 10 ppmv of benzene was found in reactor effluent gas. It is believed likely the benzene formed from hexane. Bromobenzenes were also detected in effluent gas, which can be formed by reaction between benzene and bromine (Br_2). When hexane was present in the reactor feed gas at levels suitable for combustible fluids, formation of benzene and bromobenzenes made hexane unsuitable as a combustible fluid.

Brief Description Of Preferred Embodiments

While this invention is susceptible of embodiment in many different forms, this specification and accompanying drawing disclose only some specific forms as an example of the use of the invention. In particular preferred embodiments of the invention for treatment of vent gas from a catalytic liquid phase oxidation process using compressed air are illustrated and described. The invention is not intended to be limited to the embodiments so described, and the scope of the invention will be pointed out in the appended claims.

The apparatus of this invention is used with certain conventional components the details of which , although not fully illustrated or described, will be apparent to those having skill in the art and an understanding of the necessary function of such components.

More specifically with reference to FIGURE 1, the integrated vent gas treatment system comprises: one or more oxidation vessels, illustrated as oxidation vessel **44** containing a suitable solid oxidation catalyst; vent gas heater, illustrated as exchanger **22**; and quench and/or scrubbing units, illustrated as tower **66**.

During operation of the system a vent gas stream containing volatile compounds and excess dioxygen, for example from a catalytic liquid phase oxidation process using compressed air, flows via conduit **21** into heat exchanger **22** where the vent gas stream is heated to at least a minimum catalytic conversion temperature. Nitrogen content of such a vent gas stream is, typically, more than about 90 percent by volume; dioxygen content is less than 10 percent, typically, less than about 7.5 percent; and carbon oxides and water vapor together are less than about 7.5 percent, typically less than about 5 percent. Advantageously the level of organic pollutants in the vent gas stream is substantially below the lower explosive limit at operating conditions, preferably less than about 50 percent of the lower explosive limit.

Temperatures of the heated gas are in a range upward from about 150° C, generally, in a range from about 200° C to about 600° C. The heated gas stream is transferred from exchanger **22** through conduits **25** and **33** into oxidation vessel **44**.

To facilitate catalytic oxidation of the volatile compounds, an amount of combustible fluid is admixed into the heated vent gas stream via conduit **31** or other suitable location upstream of the oxidation vessel. The amount of combustible fluid is, typically, controlled by a metering pump or flow control system (not shown). Means for controlling the amount of combustible fluid being supplied is arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures in oxidation vessel **44**.

The amount of combustible fluid can be controlled manually using conventional process instrumentation such as thermocouples to measure at least temperature of the vent gas stream upstream of the oxidation catalyst and temperature of the vent gas downstream of the oxidation catalyst and, optionally, process flow rates and gas stream compositions. However, automatic process control equipment is, advantageously, adapted for controlling the amount of combustible fluid being supplied is arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures in oxidation vessel **44**, and to limit the total amount of organic compounds in the gas to levels substantially below the lower explosive limit (LEL) at operating conditions, preferably in a range downward from about 50 percent of the LEL, and more preferably below about 25 percent of the LEL.

Using selected oxidation catalysts under suitable operating conditions, even halo-organic compounds are, advantageously, destroyed. In particular, methyl bromide is destroyed forming hydrogen bromide and/or bromine.

Temperatures of hot effluent gas from oxidation vessel **44** are in a range upward from about 200° C, generally, in a range from about 300° C to about 600° C. Hot effluent gas from oxidation vessel **44** is transferred through conduit **43** and **45** into exchanger **22**, where it is cooled by heat exchange to incoming vent gas. Effluent gas from exchanger **22** is transferred through conduit **23** into the bottom of tower **66** were the gas stream is quenched and scrubbed. A suitable aqueous solvent is fed into tower **66** through liquid feed line **51** .

Generally, the aqueous solvent comprises dilute solution of a chemical base, i.e., a substance that in aqueous solution increases the hydroxide ion concentration. The pH of these alkaline aqueous solutions is in a range upward from about 7, preferably in a range from about 7 to about 9. Where halogen containing compounds are present in the gas stream, the solvent may, advantageously, comprise additional compounds which react with halogen to enhance the scrubbing operation. Appreciably soluble oxides, hydroxides, carbonates, sulfides, etc. of the alkali metals and of calcium, strontium, barium, and ammonium ion are, generally, useful compounds. Sources of useful compounds include industrial chemicals such as lime (CaO), ammonia (NH_3), ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium formate ($NaCO_2H$), sodium sulfide (NaS), urea (NH_2CONH_2), formaldehyde (HCHO), and the like. Where compounds such as hydrogen chloride, chlorine, hydrogen bromide, and/or bromine are present in the gas stream, the aqueous solvent, advantageously, comprises dilute caustic.

A solution of soluble compounds is purged from the system via bottoms liquid line **53** to any suitable liquids/solids waste treatments. The treated gas stream is transferred from tower **66** through overhead line **63** to energy recovery and/or treatment for in plant uses, such as an inert carrier gas, or vented.

Processes in accordance with this invention achieve, typically, destruction efficiencies for carbon monoxide in a range upward from about 90 percent, preferably upward from about 95 percent or greater, efficiencies for hydrocarbons in a range upward from about 80 percent, preferably upward from about 90 percent or greater, and efficiencies for methyl bromide in a range upward from about 50 percent preferably upward from about 85 percent or more.

Operation of the system is, typically, started using air (supply not shown) and any convenient fuel supplied via conduit **71** to burner **72** to generate hot flue gas which flows from burner **72** through conduits **73** and **45** into heat exchanger **22** where an oxygen containing start-up gas stream, such as compressed air (supply not shown), is heated to at least a minimum catalytic conversion temperature, typically in a range upward from about 150° C. Other suitable sources of heat for start up include steam, hot oil, and electrical heaters. The heated start-up gas stream is transferred from exchanger **22** through conduits **25** and **33** into oxidation vessel **44**. Increasing amounts of combustible fluid are admixed into the heated gas stream via conduit **31** upstream of the oxidation vessel until effluent from the catalytic oxidation provides enough heat so that heat from burner **72** is no longer needed to maintain suitable operating conditions.

That which is claimed is:

1. A vent gas treatment system for abatement of carbon monoxide and other volatile compound emissions from an industrial process having a vent gas stream containing volatile compounds and excess dioxygen, the system comprising:

an oxidation vessel, containing a solid oxidation catalyst, disposed in the vent gas stream;

means for determining temperature of the vent gas stream upstream of the oxidation catalyst;

means for supplying an amount of combustible fluid into the vent gas upstream of the oxidation vessel to facilitate catalytic oxidation of the carbon monoxide and other organic compounds;

means for determining temperature of the vent gas downstream of the oxidation catalyst; and

means for controlling the amount of combustible fluid being delivered by the supplying means, the controlling means being arranged to provide sufficient combustible fluid for the catalytic oxidation to maintain suitable reaction temperatures in the oxidation vessel for the oxidation to form an oxidation effluent stream comprising carbon dioxide and water.

2. The vent gas treatment system according to claim 1 further comprising a gas quench and/or scrubber, disposed in the oxidation effluent stream from the oxidation vessel.

3. The vent gas treatment system according to claim 1 wherein the treatment system further comprises a gas to gas heat exchanger, disposed in both the oxidation effluent stream from the oxidation vessel and the untreated vent gas stream to transfer heat therebetween.

4. The vent gas treatment system according to claim 3 further comprising a gas scrubber, disposed in the oxidation effluent down stream of the gas to gas heat exchanger.

5. The vent gas treatment system according to claim 1 wherein the solid oxidation catalyst comprises at least one member of the group silica, alpha alumina, titania, silica alumina, zirconia and gamma alumina, and optionally at least one member of the group consisting of tungsten oxide, vanadium oxide, tin oxide, and the metals platinum, palladium and rhodium, wherein the silica, alpha alumina, titania, silica alumina, zirconia and/or gamma alumina are deposited on a ceramic or metallic honeycomb support.

6. The vent gas treatment system according to claim 1 wherein the combustible fluid comprises a member of the group consisting of carbon monoxide, hydrogen, C_1 to C_5 hydrocarbon compounds, C_1 to C_5 organic compounds containing at least one oxygen atom per molecule and mixtures thereof.

7. A process of vent gas treatment for abatement of carbon monoxide and other volatile compound emissions from an industrial process having a vent gas stream containing volatile compounds and excess dioxygen, the process comprising:

(A) Dispersing into the vent gas stream at temperatures in a range of from about 25° C to about 600° C, a controlled amount of combustible fluid selected from the group consisting of carbon monoxide, hydrogen, C_1 to C_5 hydrocarbon compounds, C_1 to C_5 organic compounds containing at least one oxygen atom per molecule and mixtures thereof;

(B) Oxidizing the combustible fluid and destroying a substantial fraction of the organic compounds in the vent gas stream by oxidation over a selected solid oxidation catalyst at temperatures in a range from about 200° C to about 600° C; and

(C) Controlling the amount of combustible fluid being delivered to the vent gas stream so as to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures for the oxidation to form an oxidation effluent stream comprising carbon dioxide and water.

8. The vent gas treatment process according to claim 7 wherein the treatment process further comprises simultaneously passing both the oxidation effluent stream from the catalytic oxidation and the untreated vent gas stream through a suitable gas to gas exchanger to transfer heat therebetween.

9. The vent gas treatment process according to claim 7 wherein the combustible fluid comprises at least one member of the group consisting of carbon monoxide, hydrogen, methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and 2-methyl-2-propanol.

10. The vent gas treatment process according to claim 7 wherein the solid oxidation catalyst comprises at least one member of the group silica, alpha alumina, titania, silica alumina, zirconia and gamma alumina, and optionally at least one member of the group consisting of tungsten oxide, vanadium oxide, tin oxide, and the metals platinum, palladium and rhodium, wherein the silica, alpha alumina, titania, silica alumina, zirconia and/or gamma alumina are deposited on a ceramic or metallic honeycomb support, and wherein an effluent stream of vent gas from the catalytic oxidation comprises carbon dioxide, water and halo acids formed by destruction of the organic pollutants.

11. A process of vent gas treatment for abatement of carbon monoxide and other volatile compound emissions from an industrial process having a vent gas stream containing volatile compounds and excess dioxygen, the process comprising:

(A) Providing a vent gas treatment system which comprises;

an oxidation vessel, containing a solid oxidation catalyst, disposed in the vent gas stream;

a gas scrubbing tower, disposed in the vent gas down stream of the oxidation vessel;

means for determine temperature of the vent gas upstream of the oxidation catalyst;

means for supplying an amount of combustible fluid into the vent gas upstream of the oxidation pressure vessel to facilitate catalytic oxidation of the organic pollutants;

means for determining temperature of the vent gas downstream of the oxidation catalyst; and

means for controlling the amount of combustible fluid being delivered by the supplying means, the controlling means being arranged to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperatures.

(B) Feeding a vent gas stream comprising carbon monoxide, volatile hydrocarbon and halogenated hydrocarbon compounds, and excess dioxygen into the treatment system, and determining temperature of the vent gas upstream of the oxidation catalyst;

(C) Supplying and controlling an amount of combustible fluid being delivered by the supplying means to provide sufficient reactants for the catalytic oxidation to maintain suitable reaction temperature in the oxidation vessel:

(D) Oxidizing the combustible fluid and destroying a substantial fraction of the organic compounds in the vent gas stream over the oxidation catalyst in the oxidation vessel to form an oxidation effluent stream comprising carbon dioxide, water and halo acid; and

(E) Contacting the oxidation effluent gas stream and a adsorption liquid in the gas scrubbing tower to form a liquid solution of soluble compounds and a treated vent gas stream.

12. The vent gas treatment process according to claim 11 wherein the combustible fluid comprises a member of the group consisting of carbon monoxide, hydrogen, C_1 to C_5 hydrocarbon compounds, C_1 to C_5 organic compounds containing at least one oxygen atom per molecule and mixtures thereof.

13. The vent gas treatment process according to claim 11 wherein the adsorption liquid is an alkaline aqueous solution comprising at least one member selected from group consisting of calcium, strontium, barium, the alkali metals and ammonium ions.

14. The vent gas treatment process according to claim 11 wherein the treatment process further comprises:

(A') Providing a suitable gas to gas heat exchanger, disposed in the vent gas up stream of the oxidation vessel; and

(E) Passing both the oxidation effluent stream and the untreated vent gas stream simultaneously through the exchanger to transfer heat therebetween.

15. The vent gas treatment process according to claim 14 wherein the combustible fluid comprises at least one member of the group consisting of hydrogen, methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and 2-methyl-2-propanol.

16. The vent gas treatment process according to claim 14 wherein the adsorption liquid is an alkaline aqueous solution comprising at least one member selected from group consisting of calcium, strontium, barium, the alkali metals and ammonium ions.

17. The vent gas treatment process according to claim 14 wherein the solid oxidation catalyst comprises titania and optionally at least one member of the group consisting of tungsten oxide, vanadium oxide, tin oxide, and the metals platinum, palladium and rhodium, wherein the titania is deposited on a ceramic or metallic honeycomb support, and wherein an effluent stream of vent gas from the catalytic oxidation comprises carbon dioxide, water, halogen acids, and elemental halogen formed by destruction of the organic pollutants.

18. The process according to claim 11 wherein the vent gas stream comprises an effluent containing organic pollutants and excess dioxygen from a chemical process of forming an aromatic acid from a corresponding methyl substituted aromatic

compound by liquid-phase oxidation of the methyl groups with dioxygen in the presence of an oxidation catalyst system at elevated pressures and temperatures.

19. The vent gas treatment process according to claim 18 wherein the adsorption liquid is an alkaline aqueous solution. comprising at least one member of the group consisting of lime, ammonia, ammonium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium formate, sodium sulfide, urea and formaldehyde.

20. The vent gas treatment process according to claim 18 wherein the combustible fluid comprises at least one member of the group consisting of hydrogen, methanol and butane.

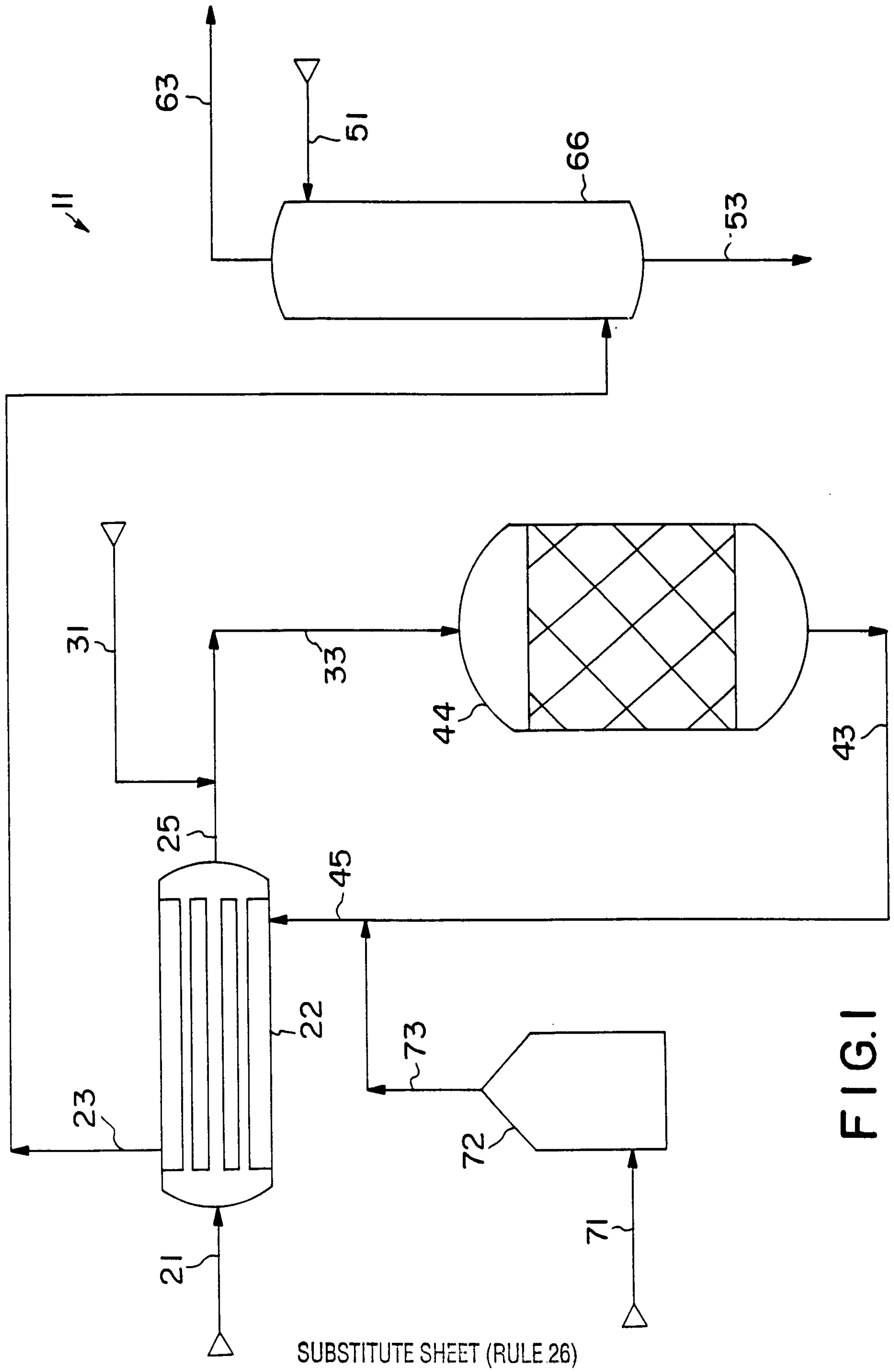

FIG.I

INTERNATIONAL SEARCH REPORT

Inten .ial Application No
PCT/US 96/07153

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 418 045 (SATO TAKAHISA ET AL) 29 November 1983 see abstract see column 2, line 21-50 ---	1-20
A	US,A,2 946 651 (HOUDRY E. J.) 26 July 1960 cited in the application see column 1, line 18-29 see column 3, line 49-52 ---	1-20
A	DE,A,39 36 744 (GUTEC GMBH) 8 May 1991 see column 2, line 32-44 ---	1-20
A	GB,A,1 485 375 (NAT RES DEV) 8 September 1977 see page 3, line 68 --- -/--	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search 20 August 1996	Date of mailing of the international search report 06.09.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Kanoldt, W

Inten .ial Application No
PCT/US 96/07153

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 407 210 (NGK INSULATORS LTD ;HIRAOKA MASAKATSU (JP)) 9 January 1991 see page 3, line 16-19 ---	1-20
A	EP,A,0 485 787 (TOSOH CORPORATION) 20 May 1992 see column 7, line 5-17; figure 1 -----	1-20

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Inten. .ıal Application No
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		JP-B- 63067090	23-12-88
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DE-A-3936744	08-05-91	NONE	
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