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# A HISTORY OF PATENTED METHODS OF OZONE PRODUCTION FROM 1897 TO 1997

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## ABSTRACT

There have been over ten thousand (10,000) United States Patents granted that are related to the generation of and applications of ozone. Over one hundred of these patents have been granted on novel techniques of ozone generation. Ozone production is predominantly achieved by one of three methods: electrical discharge methods, electrochemical methods, and ultraviolet (UV) radiation methods. Electrical discharge methods, which are the most widely used commercial methods, have relatively low efficiencies (2-10%) and consume large amounts of electricity. The other two methods (electrochemical and UV) are less cost effective. We have conducted a search of the United States Patent data base and compiled a summary of each patent granted that qualifies as a technique of ozone generation. Patents related to parts, materials, etc., of ozone generators are not included nor does the review cover the vast field related to the many applications of ozone. The commercial applications of ozone, a strong oxidizing agent, include wastewater treatment, disinfectant and odor removing applications, chemical etching, and bleaching. This ninety-two page document provides an introduction to ozone and its applications and provides a summary of the 112 U. S. Patents issued (1897-1997) on ozone generators.

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# A History of Patented Methods of Ozone Production From 1897 to 1997

## Introduction

Gaseous ozone, formed photochemically in the earth's atmosphere by radiation from the sun, is a normal constituent of the earth's atmosphere which is important in shielding the earth from cancer-causing ultraviolet radiation emitted by the sun. Large scale generation of ozone is extremely important commercially, however, due to its strong oxidizing abilities.

The word for ozone comes from the Greek word "ozein" which means "to smell" since ozone was first noticed because of its characteristic pungent odor (1). The odor is detectable in air at levels of about 0.1 parts per million, and exposure to ozone becomes fatal to humans at around levels of 100 ppm for 10,000 minutes or 10,000 ppm for 30 seconds (2). Ozone, $O_3$, is a blue-colored gas at ambient temperatures, but this color is not noticed at the low concentrations at which it is usually generated (2). In the liquid and solid states, ozone is dark blue. Liquid ozone boils at -111.3 °C and solid ozone melts at -192.5 °C (3). Ozone, which is toxic, is an unstable gas and an explosive liquid. The ozone molecule is a bent molecule with an O-O bond length of 1.278 Å and a bond angle of 116.8° as shown in the diagram below (3).

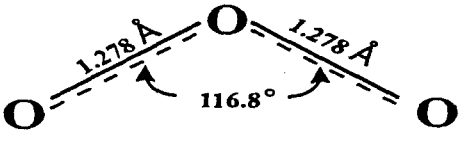


Figure 1

Second only to fluorine in its oxidizing power, ozone has many uses including but not limited to water purification, bleaching of materials such as paper, synthetic fibers, Teflon, waxes, flour, and other products, treatment of wastes in industry, deodorization and sterilization (3). Previously, chlorine products have been used for these purposes, but recent studies have shown that chlorine products may produce carcinogens such as trihalomethanes and chloramines (4). Ozone is a safe alternative to chlorine products which performs the same functions without the undesirable side effects; it is not harmful to the environment since it is made from oxygen ($O_2$) and decomposes back into $O_2$. Perhaps the most common use of commercially produced ozone is in treatment of water and wastewater. Ozone has been used in water treatment worldwide for more than 100 years (2).

Drinking water, when untreated, often contains undesirable sediments, unwanted colors, and residual tastes and odors which may be successfully removed by treatment with ozone. Treatment of drinking water with ozone disinfects the water by killing bacteria and inactivating viruses present in the water; ozone has been shown to effectively inactivate strains of poliovirus, adenoviruses, rotaviruses, and the viruses which cause vesicular stomatitis and encephalomyocarditis (4). The oxidative properties of ozone are useful in the removal of soluble iron and manganese, the removal of unwanted colors, tastes, and odors, the decomplexing of bound heavy metals, the destruction of inorganic components such as sulfides, cyanides, and nitrites, and the removal of suspended solids (2). One invention even provides a means for maintaining a degree of residual ozone in the water after treatment so that the water will remain pure during storage (5).

Ozone is also extremely useful in the treatment of wastewaters such as sewage, wastewaters associated with pulp and paper mills, and waters polluted with pesticides. The primary application of ozone in sewage treatment is disinfection, but it is also used to control odor, to aid in removal of suspended solids, and to improve the biodegradability of the wastewater (6). An advantage of ozonation of sewage is that it reduces levels of suspended solids in the effluent without the addition of dissolved chemicals, it removes viruses effectively, and it is cost-effective compared to alternate forms of treatment (2).

In the paper production industry, ozone has recently been widely considered as a method of treating pulp and paper wastewaters. These toxic wastewaters typically have high concentrations of organochlorine compounds such as chlorphenolic compounds, chloroacetones, and chloroform and are highly colored; these organochlorine compounds and colored compounds are resistant to conventional methods of treatment (6). Studies have shown that ozone is a viable alternative to chlorine-based bleaching chemicals which is effective in significantly reducing levels of organochlorines, colors, and toxicity levels in pulp and paper wastewaters. Elemental chlorine, which is usually used in pulp bleaching processes, is an effective bleaching agent but is potentially dangerous because the effluents from chlorine-based bleaching processes contain chloride by-products which are corrosive to processing equipment and which are toxic to humans and animals (7).

Industry holds several patents on environmentally improved methods of bleaching pulp with ozone. Among these patents are US Patent #5,164,043, US Patent #5,520,783, US Patent #5,174,861, and US Patent #5,451,296. Ozone is such a powerful oxidizing agent that in pulp bleaching processes, it not only bleaches the lignin portion of the pulp, but also degrades the

cellulose in the pulp (7). Wood is made up of two main components, a cellulosic portion and lignin (7). The lignin portion of wood is ideally destroyed in pulp bleaching processes, but the cellulosic portion of wood gives pulp its strength, and therefore should not be attacked by the bleaching agent (8). In order to prevent the problem of ozone attacking the cellulosic portion of pulp, the processes outlined in some patents involve using ozone as a third step in the bleaching treatment under selectively defined and carefully controlled parameters (pH control, use of chelating agents for metal ion control, pulp consistency) so that the ozone minimally degrades the cellulosic portion of the pulp (7).

Although many methods exist for producing ozone, there are three main categories of methods of ozone production, corona discharge methods, electrochemical methods, and methods involving ultraviolet radiation. In the corona discharge method, by far the most common method, oxygen or an oxygen-containing gas, most commonly air, is passed through the space between two electrodes separated by a dielectric material which is usually glass (Figure 2). The electrodes are most often either concentric metallic tubes or flat, plate-like electrodes which are connected to a source of high voltage. When a voltage is supplied to the electrodes, a corona discharge forms between the two electrodes, and the oxygen in the discharge gap is converted to ozone. A corona discharge is a physical phenomenon characterized by a low-current electrical discharge across a gas-containing gap at a voltage gradient which exceeds a certain critical value (9). First, oxygen molecules, $O_2$, are split into oxygen atoms, O, and then the individual oxygen atoms combine with remaining oxygen molecules to form ozone, $O_3$.

The corona discharge generates heat which causes the produced ozone to decompose into oxygen atoms and molecules. In order to prevent this decomposition, ozone generators which

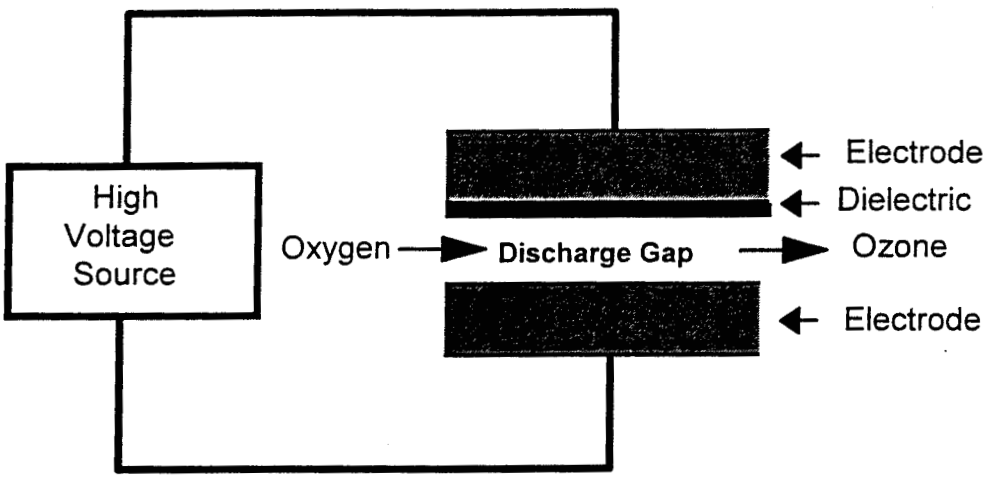


Figure 2: Schematic Diagram of A Typical Corona Discharge Ozone Generator

utilize the corona discharge method must be equipped with a means of cooling the electrodes. The temperature of the gas inside the discharge chamber must be maintained at a temperature between the temperature necessary for formation of ozone to occur and the temperature at which spontaneous decomposition of ozone occurs. This necessary cooling is usually accomplished by circulating a coolant such as water or air over one surface of the electrodes so that the heat given off by the discharge is absorbed by the coolant. Many variations of this method have been patented because it produces the highest concentrations of ozone per unit of electrical energy used.

Usually, in the electrochemical method of ozone production, an electrical current is applied between an anode and cathode in an electrolytic solution containing water and a solution of highly electronegative anions. A mixture of oxygen and ozone is produced at the anode. Another common method of ozone generation involves bombarding oxygen with ultraviolet radiation which splits oxygen molecules into oxygen atoms which combine with other oxygen molecules to form ozone. As with the corona discharge method, many modifications of the electrochemical method of ozone production and the ultraviolet radiation method exist. Many other methods of producing ozone and processes for using ozone generators have been patented.

**Discharge Methods**

**Discharge Methods Utilizing Plate Electrodes**

**Patent #577,636--February 23, 1897**

**Andreoli, Emile**. *Apparatus for Producing Ozone*.

This patent describes an apparatus for the commercial production of ozone which consists of a box formed by a series of seven metallic electrodes separated by dielectrics (see Figure 2). Oxygen passed between these electrodes is ozonized by electrical discharge between the electrodes. The goal of the invention is to maximize ozone production by maximizing the surface of the electrodes and thereby maximizing the area of the glow discharge. The invention also minimizes the temperature of operation by contacting air or oxygen only briefly with the discharge.

**Patent #955,818--April 19, 1910**

**Lohman, Anthony**. *Ozonizer*.

This patent outlines an ozone generator which consists of flat aluminum plate electrodes separated by dielectric plates. The plates are connected to terminals of an alternating current circuit, and a discharge results between the two plates resulting in conversion of oxygen to ozone in the space between the plates.

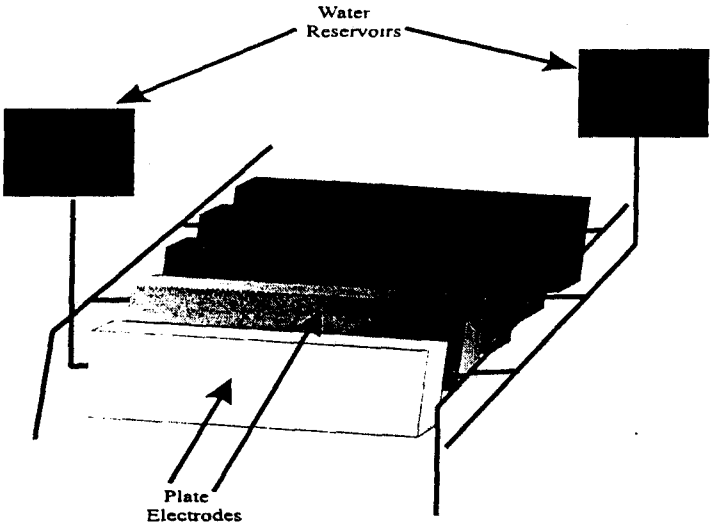


Figure 3: Diagram of Apparatus Detailed in US Patent #577,636

**Patent #2,404,778--July 30, 1946**

**Allison, Donald K.** *Apparatus for Producing Ozone.*

This patent is for a process which involves drawing air through a filter using a compressor. The air is compressed and then passed through a refrigerating unit or a heat exchanger where heat generated during compression as well as a large percentage of the water in the air are removed. The water is drained off through a drain valve. The dehydrated compressed air then passes through a valve to an air motor which drives a propeller within the ozonizing chamber of the apparatus. Inside the ozonizing chamber are sets of plate electrodes separated by

dielectric material and connected to a high voltage transformer. The electrodes are cooled by a refrigerant such as water which circulates through a refrigerant supply pipe/refrigerant return pipe system within the arrangement. The air produced by the air motor is sent into the ozonizing chamber, is circulated by the propeller, and exits the chamber through a discharge line. Electrical discharges between the plate electrodes ozonizes the compressed air within the chamber.

**Patent #3,623,970--November 30, 1971**

**Haas, Georg**. *Compact Ozonizer for Water Lines*.

This patent describes a household ozonizer which kills bacteria and removes unpleasant tastes and odors from tap water. The apparatus involves using an electrolytic cell to produce oxygen which then passes to an ozonizer. The produced ozone is then injected into water to be treated. The oxygen produced by the electrolytic cell is sent through a moisture remover before being sent to the ozonizer which consists of plate electrodes connected to a high voltage source.

**Patent #3,654,126--April 4, 1972**

**McNabney, Ralph, et al**. *Fluidized Bed Ozone Generator*.

This patent discusses an ozone generator consisting of two or more parallel plate electrodes which are covered by dielectric plates made of glass. These dielectric plates function to distribute the electrical discharge uniformly in order to avoid sparking and current surges in the ozone generator. Each electrode is connected via lead wires to the secondary of a high voltage transformer. The primary is connected to a low voltage source of AC potential. A series

of grounded electrodes, which are flat electrically conductive metallic electrodes, is spaced from the parallel plate electrodes. These grounded electrodes are hollow and water is circulated through them for cooling purposes. Oxygen or an oxygen-bearing gas is fed into the generator via a gas inlet at a pressure of about 1.6 atmospheres and enters the spaces between the electrodes. A fluidizable dielectric material such as sand, glass powder, or a powdered highly insulating plastic is contained within the spaces between the electrodes. As the oxygen gas flows through at proper rates, a fluidized dielectric bed is formed in the spaces between the electrodes. After the fluidized dielectric bed is established, a voltage is supplied to the electrodes to produce an electrical field between the electrodes. A silent electrical discharge is formed in the gaps between the electrodes, and oxygen gas streaming through these spaces is converted to ozone. The ozone-containing gas exits through an outlet and enters a separator.

**Patent #3,801,791--April 2, 1974**

**Schaefer, Richard J.** *Ozone Generator.*

This invention is an ozone generator which is made up of several pairs of plate electrodes inside a casing made of a moisture-resistant, ozone-resistant material such as silicone rubber. The use of silicone rubber reduces arcing between the electrodes and increases the lifetime of the ozone generator. The electrodes are metallic, and a pair of low-stress glass plates made of a glass other than borosilicate (Pyrex) are adhered by a moisture-resistant, ozone-resistant bonding material such as silicone rubber to the faces of the electrodes. The electrodes are positioned with the glass plates facing each other, and spacers hold the plates apart forming a chamber

through which oxygen or air may pass. A transformer is used to supply AC to the electrodes producing an electrical field which ozonizes the air between the electrodes.

Patent #3,872,313--March 18, 1975

**Emigh, Willard F., et al.** *Ozone Generator.*

This patent is a design for a plate discharge ozone generator. The ozonizer uses two groups of interleaved, relatively small reactor plates mounted inside a rectangular enclosure. The reactor plates are coated with a ceramic to form a dielectric and to prevent corrosion. Internal channels are included in the design of the reactor plates to allow a coolant to circulate inside. The enclosure in which the plates are mounted is created with two paired inlets and outlets. One of the inlet/outlet pairs allows oxygen or air to enter into the enclosure, and the corresponding outlet directs the oxygen/air/ozone mixture out of the ozonizer. The other inlet/outlet pair allows a refrigerant to circulate through the reactor plates.

Patent #3,973,133--August 3, 1976

**Emigh, Willard F., et al.** *Ozone Generator.*

This patent details an ozone generator which consists of two groups of spaced plate electrodes. The entire outer surfaces of the plates are coated with ceramic which serves as a dielectric. Channels carrying a refrigerant such as Freon run through the interior of the electrodes. This invention eliminates the use of dielectric posts used to space the plate electrodes apart. The dielectric plates are simply mounted with a small space between them. Dielectric posts used as spacers provide paths by which charges can "creep" between the plates. A "creep"

distance is defined in the patent as "the distance through which electric charges from one plate can creep toward and onto the next adjacent plate when the two plates are at different potentials." This creeping of charges between the plates stresses the ceramic coatings on the plates, the coatings eventually break down, and a massive arc-over occurs between the plates. This invention claims to increase the safety and the lifetime of the ozone generator by eliminating dielectric spacers between the plate electrodes.

**Patent #3,984,697--October 5, 1976**

**Lowther, Frank E.** *Corona Generator.*

This patent outlines an ozone generator which consists of flat plate electrodes in parallel arrangement with fired-on coatings of porcelain enamel which serve as dielectrics. The electrodes are connected to an AC voltage source of sufficient voltage to generate a corona discharge, and an oxygen-containing gas passed between the electrodes is converted to ozone by the discharge. The apparatus produces large quantities of ozone at voltages of about 6 kV. The device is air-cooled. When the dielectric constant of the porcelain enamel coating and the thickness of the coating are at optimal values, ozone production is maximized.

**Patent #4,034,229--July 5, 1977**

**Grosen, Walter, et al.** *Ozone Generating Apparatus.*

This patent is for an ozone generator which utilizes a corona discharge between plate-like electrodes arranged in a stack. The first electrode has a dielectric plate evenly spaced from both it's surfaces. A second electrode spaced from the dielectric plate is fluid cooled. A discharge in

the space between the first electrode and the dielectric and in the space between the second electrode and the dielectric converts oxygen to ozone.

**Patent #4,152,603--May 1, 1979**

**Imris, Pavel**. *Device for the Production of Ozone.*

This patent describes an ozone generating apparatus which consists of three parallel evenly spaced plate-shaped electrodes. The ozonizer consists of an electrically non-conductive housing made of PVC, glass, or some other dielectric with grooves in which the electrodes fit. A grounded electrode is connected to a high-voltage transformer which is connected to an alternating-current source. Three bipolar electrodes are placed parallel to and evenly spaced from the grounded electrode. The bipolar electrodes also have spaces between them. A discharge tube is placed parallel to, spaced from, and above the third bipolar electrode. A corona discharge is formed between the electrodes, and ozone is produced from oxygen or an oxygen-containing gas within the apparatus.

**Patent #4,320,301--March 16, 1982**

**Kogelschatz, Ulrich**. *Device for the Production of Ozone.*

This patent is for an electric-discharge ozone-producing apparatus that uses plate or tubular type electrodes. As described in the patent, the ozonator consists of two flat plate or tubular electrodes that are mounted inside a case. The side of the outer electrode which faces the inner electrode is coated with a dielectric material. On top of the nonconductive layer facing the inner electrode are mounted several electrically conducting plates. The purpose of this design is

to reduce the power consumption and increase the ozone production efficiency. To this extent, the electrically conductive plates that are mounted on top of the insulating plates are designed to form separate discharge islands. Of note is that this ozonizer is designed to work with ultra high purity oxygen.

**Patent #4,545,960--October 8, 1985**

**Erz, Gerhard J., et al**. *Fluid Treatment System and Ozone Generator Therefor.*

This patent is both a design for an air fed ozone generator and a means of using the ozone generator to purify fluids. The ozonizer uses a discharge method for the production of ozone by means of flat plate electrodes. The electrodes are housed inside an assembly such that the entire surface of the electrode is exposed to air circulating through channels. Furthermore, the electrodes are designed to prevent electrical discharge arcing and to prevent electrode degrading due to discharge arcing. The circulating pump of the generator is placed so as to accomplish the drawing of air into the reaction chamber and the mixing of air with a fluid to be treated by means of a delivery pipe that is connected to the upstream suction side of the fluid circulation pump.

**Patent #4,606,892--August 19, 1986**

**Bachhofer, Bruno, et al**. *Ozone Generator of Stack-Type Design, Employing Round Plate-Electrodes.*

This patent is a design for a water cooled ozone generator that uses stack type round plate high voltage electrodes. The purpose behind the design was to simplify the ozone generator without increasing its size and to improve the quantity of ozone that can be generated in a given

amount of time. The plate electrodes of the generator are braced counter to one another by means of two pressure plates that are located exterior of the region defined by the stacked pairs of water cooled outer electrodes. Pairs of glass plates are located in between paired outer electrodes and a counter electrode is located inside each pair of glass plates. In this manner, two discharge spaces are formed for the production of ozone from oxygen.

**Patent #4,650,648--March 17, 1987**

**Beer, Hans-Rudolf, et al**. *Ozone Generator with a Ceramic-Based Dielectric*.

This patent is a design for a plate electrode ozone generator that uses a ceramic-based dielectric. The dielectric between the two electrodes of discharge ozone generators is used to increase the power density between the electrodes and thereby increase the ability of the generator to convert oxygen to ozone. While the use of a ceramic as a dielectric is not a new concept, the nature of the ceramic that is used to provide the dielectric in this generator type is claimed to provide an improvement over generic ceramic dielectrics. The ceramic is composed of dielectric powders of different grain size that are bound together by an artificial resin. In ordinary ceramic dielectrics, there is a continuous breakdown of the ceramic due to the stresses created by the discharge. While breakdown of the fine ceramic particles also occurs with the ceramic coating used by this device, the coarser particles are more difficult to dislodge and this limits the degree to which breakdown of the finer particles can occur over a given period of time.

**Patent #4,666,679--May 19, 1987**

**Masuda, Senichi, et al**. *Ceramic Ozonizer*.

## Discharge Methods Utilizing Tubular or Cylindrical Electrodes

Patent #906,468--December 8, 1908

**Steynis, Jan**. *Process for the Production of Ozone*.

This patent is for an ozone generator which is made up of three tubular electrodes separated by dielectric plates made of glass. The electrodes are attached to a transformer which provides alternating current; this alternating current causes a silent discharge or streaming electrical discharge between the electrodes in the space between the electrodes. This space between the dielectrics and the electrodes is the ozonizing chamber into which an oxygen-containing gas is admitted. The discharge causes oxygen to be converted to ozone, and the produced ozone exits the generator via an outlet duct. A cooling liquefied gas is introduced into the hollow tube electrodes and chills the electrodes. The temperature of the gas to be ozonized remains constant as it passes through the generator because each short period of ozonization is followed by a period of cooling. This maintenance of temperature allows for the temperature to remain at the point for optimum ozone production throughout the process.

Patent #1,157,859--October 26, 1915

**Freet, William O**. *Ozone-Generator*.

This concentric tube electrode/corona discharge ozone generator uses ammonia or brine as a coolant. The apparatus uses mica as a dielectric between a stationary inner metallic cylindrical electrode and a removable outer metallic cylindrical electrode. The outer electrode is

removable so that it may be easily cleaned or replaced if it is damaged in repeated use of the ozone generator.

**Patent #1,454,219--May 8, 1923**

**Goedicke, Richard**. *Ozone-Generating Apparatus*.

This patent is for an ozone generator with concentric tubular electrodes located inside one another and spaced from one another. The electrodes are separated from each other by a glass tube which serves as a dielectric. The outer electrode is also surrounded by a glass tube. An electrical discharge between the electrodes ozonizes air which is fed into the generator. The inventor claims that water-cooling devices of this sort is insufficient due to problems such as forgetting to turn the water on and leaks in the water lines. To avoid these problems, this invention uses air to cool the electrodes. Air flows through the generator in the space inside the innermost tube of the apparatus and through the space between the outer electrode and a glass tube which surrounds it. The cooling air is also ozonized to a degree by the discharges. This partially ozonized air is recirculated through the apparatus and is finally collected with the produced ozonized air to be purified.

**Patent #1,505,669--August 19, 1924**

**Quain, John Robert**. *Apparatus for the Production of Ozone*.

This patent is for a generator which produces ozone to be used in the antiseptic treatment of wounds and for general oxidizing purposes. The ozonizer consists of concentric tube electrodes separated by a silica dielectric. Ozone is produced in the chamber between the

electrodes by electrical discharge. The outer electrode is coated with silica to prevent erosion of the electrode by ozone. The apparatus is fitted with a nozzle for applying ozone as an antiseptic to wounds.

**Patent #3,730,874--May 1, 1973**

**Trüb, Hannes**. *Tubular-Shaped Ozonizer Possessing Cooled Inner Electrode.*

This patent is for an ozone generator which consists of a tubular inner electrode and a tubular outer electrode, both made of aluminum. The electrodes are separated by a dielectric tube made of thin walled glass with a metallic coating on the inner wall. The electrodes and the dielectric tube are arranged concentrically with spaces between the inner electrode and the dielectric tube and between the dielectric tube and the outer electrode. Water or some other cooling fluid is fed into the space between the inner electrode and the dielectric tube. The space between the dielectric tube and the outer electrode serves as an ozonizing chamber. An oxygen-containing gas is fed into this ozonizing chamber, and the oxygen is converted to ozone by an electrical discharge between the inner and outer electrode.

**Patent #3,833,492--September 3, 1974**

**Bollyky, L. Joseph**. *Method of Producing Ozone.*

This patent outlines an ozonizing apparatus consisting of a several ozone generating cells of the concentric tube electrode type inside an electrically non-conductive container which is filled with a cooling dielectric liquid such as silicone oil. The container has an inlet and an outlet for the cooling liquid which continually passes through the container cooling the ozone

generating cells. The ozone generating cells consist of an inner metal tube, which forms one electrode. Water or another cooling liquid flows through the metal tube. The tube is surrounded by another tube made of a dielectric material such as glass and is spaced radially from the inner metal tube. The outer surface of the glass tube is coated with a metal which forms the outer electrode. An oxygen-containing gas passes through the space between the dielectric and the inner metal tube, and an electric discharge between the two electrodes excites the oxygen in the space to ozone which exits the apparatus through an outlet.

**Patent #3,921,002--November 18, 1975**

**Williams, Laurence O., et al.** *Ozone Generator.*

This patent is for a cryogenically cooled corona discharge ozone generator. The ozone generator outlined in the patent is cylindrically shaped with an inlet for oxygen at one end and an outlet for liquid ozone at the other end. The temperature of the generator is maintained below the boiling point of ozone so that the ozone formed by the corona discharge is condensed to a liquid before it exits through the generator's outlet. The outlet is packed with glass beads to prevent the explosive decomposition of ozone and is maintained at a thermal gradient so that gaseous ozone exits from the generator in a controllable fashion.

**Patent #3,967,131--June 29, 1976**

**Slipiec, Romuald E., et al.** *Corona Discharge Ozone Generating Unit.*

This patent is for an ozone generator comprising concentric tube electrodes. The generator consists of three dielectric tube/electrode assemblies enclosed in a cylindrical casing

made of polyvinyl chloride or another suitable insulating material. The dielectric tube/electrode assemblies consist of dielectric cylindrical tubes made of glass or a similar material, and electrodes which are connected to high voltage terminals which are connected to opposite ends of a high voltage transformer. The assembly is cooled by the air which is to be ozonized. The inner electrode is on the inner surface of the dielectric tube, and is made of a flexible, conductive piece of metal mesh material which initially does not have the same curvature as the dielectric tube. The outer electrode is made of a rigid metal mesh and is spaced from the dielectric tube forming a gap in which air is ozonized by a corona discharge between the two electrodes. The heat produced from the discharge between the electrodes causes the inner electrode to expand into contact with the inner surface of the dielectric tube.

**Patent #4,025,441--May 24, 1977**

**Tabata, Norikazu, et al.** *Ozone Generating Apparatus.*

This patent is for an ozone generating apparatus of the concentric tube electrode type. The invention consists of an inner metallic electrode surrounded by a dielectric tube. The dielectric tube is cooled by a mixture of deionized water and a glycol such as ethylene glycol or propylene glycol. The tube is equipped with an inlet and an outlet for the coolant liquid so that the liquid is continually circulated through the tube. A metallic cylindrical grounded electrode surrounds the dielectric tube and is separated from it by an annular space. This metallic cylindrical grounded electrode is cooled by water which enters through an upper inlet and exits through an outlet positioned near the lower portion of the apparatus. Air or oxygen is fed into the apparatus and enters the space between the dielectric and the outer metallic electrode. An

electric discharge between the two electrodes in this space causes the conversion of oxygen gas to ozone. The ozonized gas exits through an outlet and is collected. This apparatus differs from previous ozonizers of the same type which only provided for cooling of the outer metallic electrode because both the dielectric tube and the outer metallic electrode are cooled. This cooling prevents ozone from being converted back to oxygen by the heat of the discharge.

**Patent #4,048,668--September 13, 1977**

**von Bargen, John D.** *Electrically Driven High Voltage Ozonator.*

This patent outlines an ozone generator of the concentric tube electrode type which converts oxygen to ozone by exposing the oxygen in the space between the two electrodes to a corona discharge generated between the two concentric electrodes. The inner electrode is a hollow stainless steel tube into which oxygen gas is fed. The inner electrode is perforated with four holes through which the oxygen gas escapes into the space between the inner electrode and a concentric glass dielectric tube. This dielectric tube is in contact with the outer ground electrode which is also made of stainless steel. The oxygen gas in the gap between the dielectric tube and the inner electrode is subjected to corona discharge which is produced by applying a potential of 30 to 50 kV between the inner electrode and the ground electrode. This discharge converts the oxygen to ozone. By feeding the oxygen gas into the interior of the hollow inner electrode, the gas serves to dissipate excess heat generated by the discharge.

**Patent #4,049,552--September 20, 1977**

**Arff, John H.** *Ozone Generating System.*

This patent describes a technique for using the ozone generated from a discharge ozone generator to purify water. Specifically, the process described in this patent specifies that the water treated with this process produces water with purity high enough such that it can be used as a substitute for distilled water or as rinse solution for electroplating. The ozonizer is of the general tubular type. Included in the process is a method for introducing the ozone produced by the ozonizer into a captured body of water, and a filtration system for filtering out the fine particles produced by ozone purification. It is claimed that this method of producing purified water removes not only dissolved metals but also bacterial and viral contaminants.

**Patent #4,051,045--September 27, 1977**

**Yamamoto, Yoshihiko, et al.** *Ozone Generating Apparatus.*

This patent outlines an ozone generator with concentric tube electrodes. A glass tube which serves as a dielectric is surrounded by a metallic cylinder which is the outer electrode. An annular space exists between the dielectric tube and the metallic cylinder. A second, inner electrode is formed by adhering a vaporized metal to the inner surface of the dielectric tube. The inner electrode is connected to a high voltage terminal which supplies a rectangular waveform alternating current to the ozone generator. A discharge is formed in the space between the dielectric tube and the outer electric, and the oxygen in the space is converted to ozone. The patent claims that this rectangular waveform alternating current is more suitable for

ozone production than the typical sinusoidal waveform alternating current employed in previous methods.

Patent #4,079,260--March 14, 1978

**Dmietriev, Andrei V., et al.** *Ozone Generator.*

This patent describes an ozone generator which consists of an inner metallic cylindrical electrode with a dielectric coating of glass enamel on its outer surface (see Figure 3). Spaced from the dielectric coating is an outer electrode, two metal plates which envelope the inner electrode with the dielectric coating. The electrodes are liquid-cooled, and an electric discharge is initiated between the electrodes through an oxygen containing gas. The ozonizer has an inlet and an outlet for the cooling liquid so that it can continuously circulate through the apparatus, and it also has an inlet for oxygen or oxygen-bearing gas and an outlet for ozone-enriched gas.

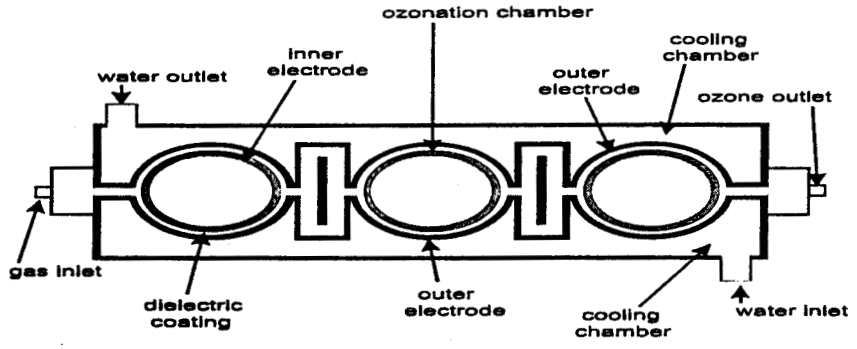


Figure 4: Schematic Diagram of Apparatus Outlined in US Patent #4,079,260

**Patent #4,101,783--July 18, 1978**

**Hutter, Felix J.** *Ozone Generator.*

This patent describes a concentric tube type ozone generator which consists of a twin-walled dielectric tube with a space between the two walls in which oxygen is converted to ozone by an electrical discharge in the space. The inner wall of the dielectric tube is in contact with an inner electrode which is made of a metallic foil such as aluminum foil or some other thin conductive material. The outer electrode is made of the same substance and is in contact with the outer wall of the dielectric tube. Oxygen gas or another oxygen-containing gas is injected into the space between the walls of the dielectric tube through an inlet, and an electrical discharge between the two electrodes formed by placing a voltage of about 20 kV across the electrodes converts this oxygen to ozone. The ozone-enriched gas exits the device through an outlet near the bottom of the dielectric tube and is either collected or may be sent to another ozone generator so that the remaining oxygen may be converted to ozone. An advantage of this device is that it incorporates a space between the inner walls of the dielectric tube in which a supply of a liquid insulating medium such as oil is housed. This oil prevents the flow of "creep currents," currents which result from dust on the walls of twin-tube type ozone generators and flow along the shortest path between the inner and outer electrodes. These creep currents can result in short circuits, damage to the high-voltage source, and injury to nearby persons. The reservoir containing an insulating medium prevents these creep currents.

**Patent #4,123,664--October 31, 1978**

**Yamamura, Takashi, et al**. *Ozone Generating Apparatus*.

The ozone generator described in this patent consists of a glass dielectric tube surrounded by a metallic cylindrical electrode which is spaced from the glass tube. An inner metallic electrode is adhered or vapor-metallized on the inner surface of the glass dielectric tube. This inner electrode is connected to a high voltage terminal. A power source connected to the high voltage terminal supplies a rectangular waveform alternating current between the two discharge electrodes. The resulting discharge between the two electrodes converts oxygen in the space between the dielectric tube and the outer electrode to ozone. This type of waveform is ideal for production of ozone because it reduces thermal and mechanical stress on the glass dielectric tube because its voltage waveform changes in proportion to the period of the current.

**Patent #4,128,768--December 5, 1978**

**Yamamoto, Yoshihiko, et al**. *Ozone Generating Apparatus*.

This patent is for a glass discharge tube ozone generator. The purpose of this invention is to increase the conversion of oxygen to ozone in commercial ozone generators by improving the discharge density between the discharge electrodes. To accomplish this, the generator described in this patent has been electrically engineered to convert alternating sinusoidal waveform current to a rectangular waveform alternating current. Included in the patent is a transformer that is designed to use a commercial power supply.

**Patent #4,159,971--July 3, 1979**

**Gneupel, Arthur**. *Ozone Generator.*

This patent is a design for an electric discharge tubular ozone generator that uses a mesh inner electrode, a solid dielectric, and a metallic foil outer electrode. As outlined in the patent, the advantage of the described ozonizer lies in the helically shaped grooves that extend in the axial direction and form a throughpass channel for the formation of ozone around the inner tube electrode. It is claimed in the patent that the helical grooves result in an increase in the efficiency of the conversion of an oxygen containing gas to an ozone/gas mixture. The design of the ozonizer also includes a means of air cooling the inner electrode by moving air through a hollow inner tube and a means of air cooling the outer electrode by attaching cooling flanges.

**Patent #4,216,096--August 5, 1980**

**Pare, Maurice, et al.** *Ozone Generation Device and Electrode.*

This patent is a design for a silent discharge ozone generator of the tubular kind. While it is not mentioned in the claims section of the patent, the discussion mentions that the electrical engineering of this ozone generator is such that it will allow an increase in voltage over other conventional designs and reduce electrode degradation by arcing and sparking. The patented design differs from other conventional tubular electrodes in the electrical engineering of an electrically conductive cap positioned in contact with the inner electrode and at one end of the generator tube. The cap is cylindrically shaped and extends into a conical portion. It is claimed in this patent that the design of the cap causes a reduction in the concentration of lines of force in its area.

**Patent #4,234,800--November 18, 1980**

**Kenly, William L.** *Ozone Generator.*

This patent is for a modular ozone generator in which ozone is formed by corona discharge. The ozonator is tubular in design and consists of a central fluid-cooled metal electrode surrounded by an intermediate tubular dielectric material that has an outer metallic coating and is designed to serve as an outer electrode. Furthermore, the outer dielectric/electrode is designed to be surrounded by a jacket through which a cooling oil circulates. The main purpose of this design is to simplify the construction of the general type of ozone generator described by the apparatus and to reduce construction costs and breaking.

**Patent #4,383,976--May 17, 1983**

**Notaro, Salvador P.** *Ozone-Generating Assembly.*

This patent is a design for an electric discharge ozone production apparatus that makes use of a plurality of generator tubes that are mounted parallel with respect to one another and are connected together by perpendicular rods that serve to provide electrical connections and support to the generator tubes. The individual generators are made up of rod electrodes on the interior of the tube that comprise the inner tube electrode of the generator and the tube is covered by a cylindrical casing of metal mesh that comprises the outer tube electrode. Air or oxygen is fed into the tops of each of the generator tubes by tubing that is connected to an air distributor that has the potential to feed gas into a number of discharge tubes simultaneously. The lower rod of the discharge tubes which serves to provide both support and electrical connection to the individual discharge tubes is hollow. Gas that is fed into the tops of the ozone generators exits

the generator by a connection between the generator and the hollow bottom support rod. In this manner, the ozone that is produced by the assembly can be collected at one location and then be fed to any desired location. The advantages of this apparatus over other industrial scale ozone generators is that the use of a battery of smaller ozone generators instead of a "giant ozonizer" avoids the problems associated with the high voltages that are required by the "giant ozonizers."

**Patent #4,411,756--October 25, 1983**

**Bennett, Douglas L., et al.** *Boiling Coolant Ozone Generator.*

This patent is a design for a boiling coolant corona discharge ozone generator. Oxygen is fed into a cylindrical electrode/dielectric/electrode assembly where the corona discharge causes the reaction that converts some of the oxygen to ozone. The oxygen/ozone mixture is then directed out of the generator. The reaction chamber is housed inside a rectangular assembly which contains a cooling fluid and a condenser. The heat created by the ozonizer is transferred to the cooling fluid which in turn boils. The gas phase coolant is then condensed by a water fed condenser so that it is recycled. This patent claims that the cooling method increases the efficiency of the conversion of oxygen to ozone.

**Patent #4,417,966--November 29, 1983**

**Krauss, Ralf, et al.** *Apparatus and Method of Producing Ozone.*

This patent is a design for both an apparatus and method for a geometrically cylindrical ozone generator that uses a "plasma electrode", a second annular electrode, and an insulating material between the two electrodes. The "plasma electrode" as described in the patent is formed

by sealing a metal electrode inside a glass/Pyrex/quartz tube that has an internal atmosphere which consists of an ionizable gas. Between the "plasma electrode" and the outer annular electrode there is a space containing an air inlet and outlet that allows for an oxygen containing gas to flow and be converted to an ozone/gas mixture. As mentioned in the discussion of this patent, this type of generator shows an increase in the efficiency of the conversion of oxygen to ozone. Also discussed are several advantages that this design has over other discharge ozone generators, including but not limited to the production of less heat and the protection against electrode oxidation.

**Patent #4,461,744--July 24, 1984**

**Erni, Peter, et al.** *Apparatus for Generating Ozone by an Electrical Discharge.*

This patent outlines an apparatus for generating ozone by electric discharge. The apparatus is a tube ozonizer consisting of an outer metal tube that forms one electrode with a glass tube inside and an electrically conductive layer coating the inside of the glass tube and forming the second electrode. The apparatus uses pulse discharges to form ozone by creating a plate-like spark gap. According to the claims, the pulse production method leads to an increase in the efficiency of the conversion of oxygen to ozone, and it is possible to convert conventional AC ozonizers to pulse operation.

**Patent #4,504,446--March 12, 1985**

**Kunicki, Wojciech, et al.** *Ozone Generator.*

This patent is an outline for a tubular ozone generator. The generator uses a discharge method for the production of ozone in which an outer metal tube forms one electrode, a glass tube forms a dielectric, and a metal coating on the interior of the glass tube forms the second electrode. The discharge method uses a high-frequency AC source. Included in the design is a method for air cooling the inner electrode by using a heat dissipating metal body inside the inner electrode which also has the potential for serving as the electric connection for connecting the inner electrode to the voltage source, and a method for air cooling the outer electrode by attaching metal cooling flanges.

**Patent #4,614,573--September 30, 1986**

**Masuda, Senichi.** *Method for Producing an Ozone Gas and Apparatus for Producing the Same.*

This patent is a design for an oxygen fed ozone generator that uses an electric discharge method for the production of ozone. As discussed in the patent, the design of the discharge device is in the form of two cylindrical electrodes that have an alumina ceramic dielectric between them. This design is unique in that it includes a method for increasing the density of the oxygen gas that is in the ozonizer. The density of the gas in the ozonizer is increased by means of a pressurizing pump and two types of cooling fins that are attached to the electrodes. Of the fins that are attached to the electrodes, some of them are air cooled and some are designed to allow for a cooling fluid to circulate in the interior of the fin. It is claimed in this patent that the

increase in the density of oxygen in the ozonizer results in a 5% conversion efficiency of oxygen to air.

Patent #4,640,782--February 3, 1987

**Burleson, James C.** *Method and Apparatus for the Generation and Utilization of Ozone and Singlet Oxygen.*

This patent is an outline for both a method of producing ozone and singlet oxygen and a process to use the ozone and singlet oxygen to sterilize surgical instruments/containers and kill pathogens on the surface of the skin. The production process involves circulating oxygen into a cylindrical discharge area formed by a cylindrical outer electrode, a cylindrical solid dielectric spacing , and a cylindrical interior electrode. After the oxygen gas flow passes through the reaction chamber, the ozone, singlet oxygen/oxygen flow is directed towards the instruments/containers for sterilization or towards the surface of skin for the purpose of killing pathogens.

Patent #4,650,573--March 17, 1987

**Nathanson, Roger T.** *Ozone Generator Water Treatment.*

This patent is for an ozone generator consisting of a metal "brush" which forms an inner electrode in a concentric tube electrode arrangement. The brush is surrounded by an ozonizing space which is bounded by a Pyrex glass cylinder which functions as a dielectric between the brush electrode and an outer cylindrical electrode made of sheet metal. Corona discharge between the two electrodes converts oxygen in air which is fed into the apparatus to ozone which

is collected outside the ozonizing chamber. The patent involves a method for water purification using the produced ozone. The method entails a means of automatically activating the ozone generator in response to water flowing through the use of an aspirator in conjunction with a faucet or in response to activation of a well pump.

**Patent #4,656,010--April 7, 1987**

**Leitzke, Ortwin, et al**. *Device for Producing Ozone.*

This patent is a design for a tubular high voltage discharge ozone generator. This design is unique in that it uses a small inner electrode with a diameter that is one-half the diameter of the outer electrode. The design for the inner electrode includes diameters from 0.5 to 10 mm, and the inner electrode is constructed from either a single wire or a plurality of wires. A plastic, glass, or Pyrex dielectric separates the inner electrode from the outer electrode and creates the region through which oxygen or oxygen containing gas flows. A second design is included in this patent which uses a generator built along the same principles but with parabolic shaped electrodes to allow a cooling fluid to circulate along the exterior of the outer electrode. This patent claims that this type of ozone generator can be used to create a uniform charge density between the inner and outer electrode as opposed to other types of tubular discharge ozone generators and thereby increase the efficiency of the process which converts oxygen to ozone.

**Patent #4,690,803--September 1, 1987**

**Hirth, Michael**. *Ozone Generator.*

This patent is an improvement of the concentric tube electrode corona discharge ozone generator. The inner metallic electrode is covered with a dielectric material of titanium dioxide ceramic or of plastic filled with a dielectric powder. Between the dielectric material and the outer electrode is a discharge gap in which corona discharge between the two electrodes converts oxygen to ozone. The surface of the dielectric layer facing the discharge gap is coated with a protective glass or ceramic layer of silicon dioxide. This protective coating makes the ozone generating apparatus more resistant to stresses caused by the discharge.

**Patent #4,696,800--September 29, 1987**

**Sasaki, Toshihiko, et al**. *Ozone Generating Apparatus.*

This patent is a design for a safe and compact high voltage ozone generator. The design of the generator includes a casing in which all parts of the ozone generator are mounted. A transformer is mounted inside the casing and is connected to the discharge apparatus. The outer electrode of the discharge apparatus is in the form of a rectangle in which one end is closed and the other end left open. The inner electrode consists of a parabolically shaped glass discharge tube with an interior coating of an electrically conductive material. Included in the design of the electrodes are grounding connections, transformer connections, a gas inlet, and a gas outlet.

**Patent #4,725,412--February 16, 1988**

**Ito, Hajime**. *Ozone Generator*.

This patent is a design for an electric discharge ozone generator that is engineered so that the ozone/gas mixture produced by the generator is not contaminated with particles that are the result of electrode degradation. This type of generator is designed to be used in industrial situations that require a clean room. The apparatus described by this patent is formed by two electrodes that are made by starting with either quartz or silica tubes and depositing an electrically conductive material on the exterior of the outer electrode and the interior of the inner electrode by metallic vapor deposition. In this manner, the discharge area between the two electrodes is not in contact with the metallic electrically conductive material that forms the electrodes. In addition, the outer electrode coating is designed to be made from a water resistant material so that electrically nonconductive pure water can circulate in direct contact with this electrode for cooling purposes.

**Patent #4,764,349--August 16, 1988**

**Arff, John H., et al**. *Ozone Generator*.

This patent is a design for a high voltage electric discharge ozone generator. The design itself consists of a sealed glass tube that is filled with a gas that when subjected to high voltage will produce a radiation of energy through the tube. A high voltage on the interior of the glass tube is accomplished by longitudinally mounting a conductive metallic rod inside the glass tube such that the rod perforates one end of the tube while maintaining an atmospheric seal. The outer electrode of the ozone generator has undergone extensive engineering and does not resemble the

common plate or tube electrode that is characteristic of many ozone generators. Instead, the outer electrode is a sleeve of flute like perforations that surrounds the glass tube. It is on the interior of the flute-like perforations that ozone is formed by this apparatus. This design is intended to provide a simplistic and inexpensive method for producing ozone.

Patent #4,877,588--October 31, 1989

**Ditzler, Lee C., et al.** *Method and Apparatus for Generating Ozone by Corona Discharge.*

This patent is for a corona discharge ozone generator that is designed to add the ozone produced from an oxygen containing gas to a body of captured water. Furthermore, the outlined apparatus also includes a method for monitoring and controlling the content of ozone in the captured water by means of a device that reads the oxidation-reduction potential of the water. The outlined apparatus consists of a metallic inner electrode connected to electrified radial brushes that come into contact with bands of dielectric material that alternate with cooling regions. The metallic inner electrode defines the axis of the ozone generating apparatus which is of cylindrical design. The alternating corona discharge and cooling regions are achieved by surrounding the circular dielectric bands in contact with the radial brushes with an outer cooling wall that is in contact with a coolant liquid such as water.

Patent #4,886,645--December 12, 1989

**Fischer, Melchior, et al.** *Ozone Generator.*

This patent is for a stack type modular discharge ozone generator. As described in the patent, the outer electrodes are of the water cooled tubular type. Furthermore, the tubular outer

electrodes are vertically stacked with respect to one another while the axis of each individual tubular outer electrode is horizontal with respect to the tank that contains all of the inner and outer electrodes. The modular inner electrodes are formed from a dielectric material and a metallic coating. A number of the modular inner electrodes are placed in series in between two outer electrode plates to form a discharge gap for the production of ozone. The purpose behind the construction of this ozone generator was to provide a means for producing the quantities of ozone needed in industrial situations.

**Patent #4,960,569--October 2, 1990**

**Fovell, Richard C., et al**. *Corona Discharge Ozonator with Cooled Flow Path.*

This patent is for an ozone generator of the concentric tube electrode corona discharge type (see Figure 4). The invention consists of the typical inner metallic cylindrical electrode made of tungsten or stainless steel, typical outer electrode made of aluminum, steel or copper, and the typical dielectric made of borosilica glass. The ozonation chamber is formed between the dielectric and the outer electrode; corona discharge in this chamber formed by applying a high voltage across the electrodes ozonizes the oxygen within the chamber. This invention also comprises a plurality of spherical solids made of an ozone-resistant metal which line the ozonation chamber which is the space between the outer electrode and the dielectric. The spheres function to transfer heat by direct thermal conduction from the hot dielectric material and inner electrode to the cooler outer electrode.

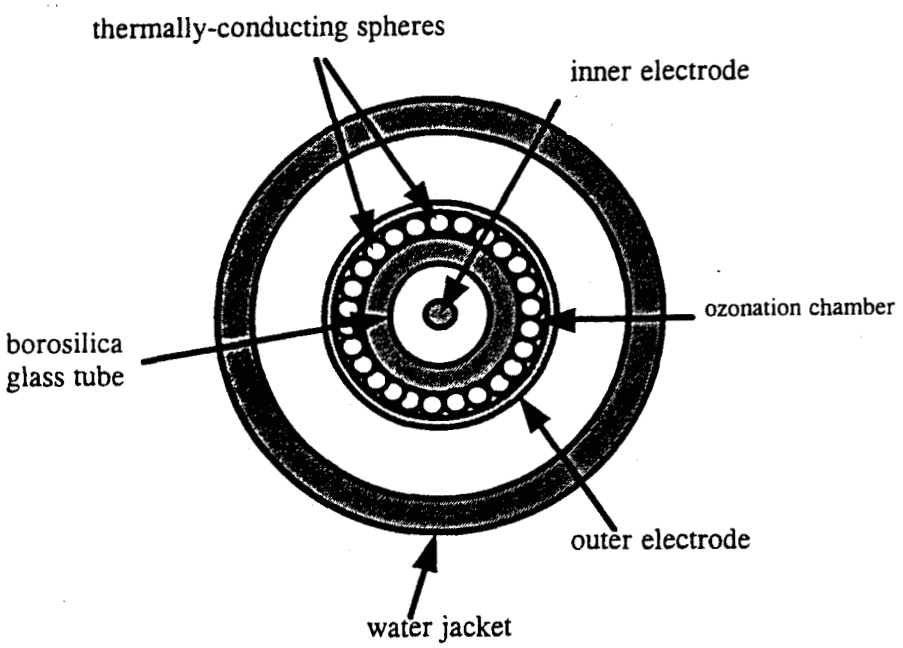


Figure 5: Diagram of Apparatus Detailed in US Patent #4,960,569

**Patent # 4,981,656--January 1, 1991**

**Leitzke, Ortwin**. *Device for the Production of Ozone.*

This patent discusses an apparatus for production of ozone involving two electrodes which are concentric tubes. A silent electrical discharge oxidizes gases in a chamber between the two tubes to produce ozone. The internal electrode is a voltage-conducting hexagonal bar or hexagonal tube, the outer electrode is a circular metal tube which is either water-cooled or air-cooled, and the ratio of the diameter of the external electrode to the diameter of the internal electrode is not greater than two. The inner electrode is surrounded by a gas discharge chamber;

this gas discharge chamber is surrounded by a dielectric which is a glass tube. The dielectric is then surrounded by another gas discharge chamber which is in contact with the external electrode. In previous inventions of similar design, the ratio of the diameters was greater than two. The inventor claims that the smaller ratio (which reduces the distance between the two electrodes) results in a lesser field intensity or voltage required for the silent electrical discharge; this decrease in field intensity or voltage required to produce the discharge increases the degree of efficiency of the type of device consisting of concentric tubular electrodes.

**Patent #5,004,587--April 2, 1991**

**Tacchi, Ernest J.** *Apparatus and Method for Ozone Production.*

This patent details an ozonizer chamber consisting of a flexible high tension electrode with supporting spacers which are enclosed within a flexible dielectric tubing. The dielectric tubing separates the high tension electrode from a fluid counter-electrode which surrounds the outside of the dielectric tube. A dry oxygen-bearing gas passes through and is stored inside the tube; electrical discharges occur between the high tension electrode enclosed by the dielectric tube and the fluid counter-electrode which completely surrounds the dielectric tube, and ozone is produced by oxidization of the oxygen-bearing gas. The fluid counter-electrode used is of high electrical conductivity so that it functions as an electrolytic power connection to the gas discharge chamber by changing electron current to ion current and is also a means of heat removal. The ability of the fluid counter-electrode to absorb thermal energy by conduction is an advantage since elevated temperatures caused by the electrical discharges lead to more rapid decomposition of the produced ozone.

**Patent #5,008,087--April 16, 1991**

**Batchelor, Douglas R.** *Ozone Generator Apparatus and Method.*

This patent outlines an ozone generating apparatus of the type involving concentric tube electrodes with a middle dielectric member. The device described in this patent consists of an inner electrode made of stainless steel which is hollow to effect more efficient cooling of the electrode, a middle dielectric member made of a glass material such as borosilicate, and an outer electrode made of stainless steel. The device is enclosed in a housing with a much larger diameter than the outer electrode so that a jacket through which water is introduced as a coolant can be inserted in the space. The chambers between the inner electrode and the dielectric member and the outer electrode and the dielectric member serve as gas discharge chambers so that applying a high voltage between the inner and outer electrodes produces a corona discharge of the gas through the dielectric member which creates ozone. One end of this device is sealed to enable feed gas traversing the gap between the inner electrode and dielectric member to reverse direction and traverse the gap between the dielectric member and the outer electrode thus producing additional ozone as the gas travels between the dielectric and the outer electrode. The created ozone is collected from an outlet when the gas returns to its starting point. The reversing of the gas flow cools the outer surface of the dielectric which reduces the difference in temperature between the inside and the outside of the dielectric; this reduction in temperature difference decreases stress on the dielectric and lengthens the life of the apparatus.

**Patent #5,034,198--July 23, 1991**

**Kaiga, Nobuyoshi, et al.** *Ozone Generator and Ozone Generating Method.*

This patent discusses an ozone generating device which consists of a dielectric tube with an inner-surface stainless steel coating between 2,000 Å and 5,000 Å thick. The stainless steel coating serves as the inner electrode in the water-cooled concentric tube electrode arrangement. The outer electrode is also made of stainless steel and serves as a grounding electrode. An oxygen-containing gas is fed into the device via a feed gas inlet, and the gas passes between the two electrodes which are connected to a high-frequency power source. The high-frequency power supplied to the stainless steel film by the source causes a silent discharge between the dielectric tube with the stainless steel coating and the outer cylindrical grounding electrode. The oxygen molecules in the gas are excited by the discharge to form ozone gas. The gas is then expelled from the chamber through a gas outlet. The inventors claim that the invention has the advantages of having an increased ozone generation amount per unit volume due to the high-frequency electric power supplied by the power source, high resistance of stainless steel against erosion by nitric acid which is formed when nitrogen oxides react with moisture in air and high resistance against erosion by ozone itself. The thickness of the stainless steel coating on the inside of the dielectric tube is ideal in that it is resistant to peeling due to repeated heating and cooling of the ozonizer.

**Patent #5,093,087--March 3, 1992**

**Freeman, Michael D.** *Ozonator Apparatus.*

This patent outlines an ozonator of the concentric tube electrode type. The ozonator

comprises a conductive rod inside an outer metallic housing. The conductive rod is surrounded by a polymeric tube, and the ozonizing chamber is formed between this polymeric tube and a polymeric housing on the inside of the outer metallic housing. A twelve-volt coil with a positive terminal and a negative terminal and a coil output socket is in contact with the inner conductive rod. A battery with a positive and a negative twelve-volt cable is connected to the terminals of the twelve-volt coil, a source of 110 volt alternating current which is attached to a voltage regulator, and a capacitor bank are linked together to produce a discharge in the ozonizing chamber which excites oxygen to ozone. The device has the advantages of being compact, economical, and easy to use.

**Patent #5,124,132--June 23, 1992**

**Francis, Jr., Ralph M., et al.** *Corona Discharge Ozone Generator.*

This patent is for a tubular plasma discharge ozone generator. The ozonator described in this patent has a hollow metal cylinder in which a sealed glass tube is mounted so as not to touch the cylinder walls. The sealed glass tube is filled with an ionizable gas, and is connected to wire leads at both ends. Together, the outer metal cylinder and the sealed glass tube are designed to form the outer and inner electrodes for a discharge ozone generator. Oxygen containing gas is introduced into the apparatus between the outer and inner electrodes at one end of the tube and the ozone/oxygen containing gas is collected at the other end.

**Patent #5,145,653--September 8, 1992**

**Fischer, Melchior, et al.** *Device for Generating Ozone.*

This patent describes an ozone generator consisting of a plurality of concentric tube type ozone generators inside a casing. Each generator consists of an outer tubular metallic electrode inside which is a segmented inner electrode coated with a dielectric. The segments are supported and spaced independently from one another inside the outer electrode. A tension rod through the middle of the segmented inner electrode connects the segments and supplies power to the ozone generator. The segmenting of the electrode ensures accurate spacing between the electrodes because it eliminates the problems of dimensional deviation and bending.

**Patent #5,268,151--December 7, 1993**

**Reed, Bruce A., et al.** *Apparatus and Method for Generating Ozone.*

This patent details an ozone generator of the concentric tube electrode type. The inner electrode is a stainless steel tube which is surrounded by a glass dielectric tube separated from the stainless steel tube by non-conducting spacers forming a chamber for air to pass through. The glass tube is coated with a graphite dispersion in liquid which dries in a uniform, conductive layer. This outer coating of graphite serves as the outer electrode. Oxygen or an oxygen-bearing gas is introduced into the chamber between the inner electrode and the glass dielectric through holes in the upper portion of the inner stainless steel tube, and a corona discharge is formed in the gas by a pulsed electrical signal. The discharge splits apart $O_2$ molecules to form oxygen atoms which may then recombine with $O_2$ molecules to form $O_3$. The ozone exits the generator through holes in the downstream end of the inner stainless steel tube.

**Patent #5,411,713--May 2, 1995**

**Masao, Iwanaga**. *Ozone Generating Apparatus*.

This patent is for a method of ozone production that uses discharge electrodes as the ozone generators. The outlined process uses a series of the ozone generators that are stacked on top of one another and are spaced in such a way so that the oxygen or oxygen-containing gas that enters into the ozone generating apparatus must pass successively through each individual generator. The individual generators themselves consist of a water cooled outer tubular electrode with a dielectric spacing and an inner linear electrode. Furthermore, the decreasing voltage differential occurs along the arrangement of electrodes in the direction of the gas flow.

**Miscellaneous Discharge Methods**

Patent #2,876,188-- March 3, 1959

**Thorp, Clark E., et al.** *Ozone Manufacture.*

This patent is a design for an industrial ozone production process that uses glow discharge for the purpose of converting oxygen to ozone. As outlined by the patent, oxygen supplied from tanks enters into the device at subatmospheric pressures and first passes through a purification step such as a combustion tube. The oxygen then travels through a liquid oxygen cooled carbon dioxide and water trap before passing through a rotameter. After purification, the oxygen is converted to ozone and then collected in a liquid nitrogen cooled ozone collector. The remaining oxygen is then recycled back into the ozonizer. This process claims high results in increasing the conversion efficiency of oxygen to ozone and the efficient use of the energy supplied to the ozonator.

Patent #3,856,671 December 24, 1974

**Lee, Hanju, et al.** *Closed-Loop Ozone Generating and Contacting System.*

This patent outlines a closed-loop system for generating ozone to be used in water treatment. A feed gas, usually ambient air, is sent through a pressure-swing fractionator, a device which removes nitrogen from air and results in an oxygen-enriched gas mixture which is between 30 and 95 percent oxygen. The oxygen-enriched mixture then flows to an ozonator which is made up of either tubular electrodes or flat electrodes. The oxygen-enriched gas passes between the pairs of electrodes and electrical discharge between the electrodes produces ozone from the

oxygen-enriched gas. The mixture of ozone/oxygen-enriched gas that results is then brought into contact with water to be treated. Nitrogen from air as well as from waste decomposition is dissolved in the water to be treated, and this nitrogen mixes with the excess oxygen-enriched gas that is passed over the water. The mixture of oxygen-enriched gas and ozone is then recycled back to the pressure-swing fractionator which removes the nitrogen, and the process is repeated. In previous methods of water purification, a complex deaeration step was necessary before treatment of the water. This deaeration step eliminated nitrogen build-up in closed-loop systems. With the pressure-swing fractionator, this deaeration step is not necessary.

**Patent #3,865,733--February 11, 1975**

**Taylor, Leland Thomas.** *Apparatus for the Production of Ozone.*

This patent describes an ozone generator which consists of two or more wires woven together as a "fabric" of wires; the wires serve as electrodes. The wires are made of copper, brass, aluminum, or any other conductive metal and are coated with a thick coating of a non-conducting material, such as Teflon, which is inert to ozone. Oxygen gas or an oxygen-containing gas is fed into the generator perpendicular to the wires, and a corona discharge formed between the wires converts oxygen in the spaces between the wires to ozone.

**Patent #3,905,920--September 16, 1975**

**Botcharoff, Jacqueline W.** *Ozone Generating Device.*

This patent is a design for an ozone generating apparatus that can be plugged into a car's cigarette lighter. The device is designed to provide a means for transforming the D.C. current of

a car's battery into A.C. current for the purposes of raising the relatively small voltage of the car's battery. While the patent suggests using electrically generated ionizing radiation for the purpose of ozone formation, it does not exclude using discharge or UV methods for accomplishing ozone production. This device is designed to produce ozone at small non-toxic levels that can be used to deodorize the interior of a car.

**Patent #3,963,625--June 15, 1976**

**Lowther, Frank E.** *Ozone Generation and Recovery System.*

This patent outlines a system for the generation and recovery of ozone. The system consists of several ozone generators of the corona discharge type separated by cooling devices. The ozone/oxygen mixtures are cooled between each ozone generator. A pressure-swing device is used to separate air into oxygen and nitrogen. This oxygen-rich gas is passed through the series of ozone generators and cooling devices, and oxygen is converted to ozone in a concentration not greater than one weight percent. The oxygen/ozone mixture is then contacted with a solid adsorbent such as silica gel which adsorbs the ozone. The purified oxygen gas may then be recycled to the ozone generator and the process repeated. The nitrogen initially separated from air is used to desorb the ozone from the silica gel.

**Patent #4,035,657--July 12, 1977**

**Carlson, Curt William.** *Ozone Generator.*

This patent is for an apparatus which produces ozone and then injects it either into swimming pool water or air to be treated by the ozone. The ozonizer consists of an inner and an

outer electrode made of rectangular sheets of stainless steel wire mesh. The inner electrode is surrounded by an inner dielectric member, and the outer electrode has an outer dielectric member on its inner surface. The two dielectric members are separated by a helical spacer. Ozone is formed by a silent electrical discharge in the gap between the two dielectric members from oxygen gas or air injected into the apparatus. Several of these ozonizers are connected in series so that the yield of ozone is increased. The ozone is immediately injected into water or air for treatment.

**Patent #4,062,748--December 13, 1977**

**Imris, Pavel.** *Method and Apparatus for Producing Ozone.*

This patent is for an ozone generator which utilizes a corona discharge between two electrodes housed in a dielectric casing made of PVC. Three electrodes are located inside the casing, a discharge electrode, a grounded counter-electrode, and a bipolar electrode. The discharge electrode and grounded electrode are connected to a high-voltage DC generator. A corona discharge forms between the electrodes and ozonizes the oxygen within the apparatus.

**Patent #4,140,608--February 20, 1979**

**Vaseen, Vesper A.** *Converting Oxygen to Ozone Using a Liquid Dielectric Containing Dissolved Oxygen.*

This patent describes a method of ozone production involving a corona discharge between two electrodes spaced by a dielectric liquid such as a fluorocarbon. The liquid acts not only as a dielectric, but also carries dissolved oxygen-bearing gases through the corona discharge

area so that the dissolved oxygen is converted to ozone. The liquid also serves to dissipate the heat produced by the discharge. The liquid used should be non-miscible with water, non-toxic to bio-organisms, non-oxidizable with ozone, and should have an affinity for dissolving oxygen. Oxygen should be dissolved in the liquid at pressures above atmospheric pressure. The ozone dissolved in the dielectric liquid can then be released from the dielectric for immediate use by decreasing the pressure on the liquid. An alternative method for utilizing the produced ozone is to mix the dielectric liquid, still under pressure, with wastewater to be treated, and then release the pressure. The ozone is released into the wastewater, and the dielectric liquid, since it is non-miscible with water may be separated from the water.

**Patent #4,351,734--September 28, 1982**

**Kauffman, Gilbert**. *Spark Cell Ozone Generator.*

This patent is an outline for an ozone production process that generates ozone in a stream of moving liquid waste. The invention consists of a lower inlet which allows waste water and oxygen enter the device. Inside the ozonizer there are two complementary electrodes with electrically conductive particles packed between them. As waste water and oxygen enter the device, the packing material expands to establish electrical contact between the electrodes which creates localized arcing between the particles that make up the packing material; this arcing converts oxygen to ozone which treats the wastewater. The water then flows out of the device through an upper outlet.

**Patent #4,386,055--May 31, 1983**

**McBride, Thomas D.** *Ozonator with Air Actuated Rotor.*

This patent is a design for an oxygen-fed ozone generator that uses a corona discharge method to convert oxygen to ozone. The design of the device is such that air coming into the ozonizer is used to rotate windmill-like blades. The blades have conducting capability and are spaced such that they can rotate freely inside the reaction chamber. Furthermore, as the blades rotate, their edges come in close proximity to adjustable spaced multi-conductors to produce a corona discharge. It is claimed by this patent that the movement of the conducting blades causes cooling which in turn decreases electrode degradation.

**Patent #4,462,965--July 31, 1984**

**Azuma, Kenkoku, et al.** *Intermittent Ozonizing Apparatus.*

This patent is a process for using an oxygen fed intermittent ozonizing apparatus that uses a discharge method for the treatment of coolant water. Oxygen is fed into a reaction chamber where it is converted into an oxygen/ozone mixture. From the reaction chamber, the oxygen/ozone gas is directed toward an adsorption tower where the ozone is adsorbed from the gas mixture. The oxygen is then recycled back into the ozonizer reaction chamber. The adsorbed ozone is desorbed by means of suction under low pressure and directed toward an ozone outlet. The purpose behind using ozone in coolant water is to prevent the buildup of organic material on the interior of circulating pipes.

**Patent #4,790,980--December 13, 1988**

**Erni, Peter, et al.** *Device for the Generation of Ozone and a Process for its Operation.*

This patent is both a design for the electric discharge generation of ozone and an operating process. As described by the author of the patent, the design calls for an ozone generator with two electrodes connected across the secondary winding of a high voltage transformer. The primary winding of the transformer is connected to a converter which supplies square wave current with variable amplitude and frequency. A compensation coil is connected across either the primary or the secondary of the transformer. The ozone generator uses a solid dielectric and a has gas path between the two electrodes. As claimed in the patent, the result of the electrical engineering of this generator is an improvement in the power factor of the ozone generator at relatively high current frequencies.

**Patent #4,909,996--March 20, 1990**

**Uys, Richard.** *Ozone Generator.*

This patent describes a modular ozone generating device of the discharge type that is designed to be used to produce the quantities of ozone needed to purify a local environment. The ozonating device consists of a container that is longitudinally divided into two compartments. One of the compartments contains a number of transformers that are placed side by side and a device that is used to force air into the compartment for the purpose of cooling the transformers. The second compartment contains a number of electrostatic ozone generators that are equal in number to the number of transformers in the first compartment. Each electrostatic ozone generator is paired to one of the transformers in the first compartment with electrical connections

between the transformer and generator. The second compartment also contains an opening at the far end of the air blowing device that allows the air traveling in the first compartment to travel into the second compartment before it leaves the container.

**Patent #4,992,246--February 12, 1991**

**Serizawa, Yoshikiyo.** *Ozonizer.*

This invention simplifies the corona discharge ozonizer by using as one of the electrodes a set of metallic blades which rotate inside a metallic casing which forms the other electrode. The rotation of the blades blows the air through the apparatus so that cooling of the electrodes results. The fan-like electrodes also eliminate the need for additional devices to blow air into the ozonizer and to pump the ozone out of the chamber. The ozone produced is simply exhausted outside the apparatus by the rotating blades. The metallic casing has on its inner surface a dielectric member made of silicone rubber. The electrodes are attached to a high voltage source of 10 kV-15 kV which causes a corona discharge between the casing and the metallic-blade electrodes, and ozone is formed from the oxygen within the chamber.

**Patent #5,047,127--September 10, 1991**

**Tottori, Isao, et al.** *Ozone Generating Method.*

This patent outlines a method for increasing quantities of ozone produced by a conventional ozone generator which uses a silent discharge in oxygen gas. The claims are that mixing oxygen gas with nitrogen gas in a ratio of oxygen to nitrogen of 1:0.0002 to 0.02 increases the efficiency of the ozone generating device because nitrogen acts as a catalyst to the

reaction. In concentrations of nitrogen above 0.02 or below 0.0002, the catalyzing effect is not observed. A greater concentration of produced ozone was observed when nitrogen gas in the concentration range of 0.0002 to 0.02 was mixed with the oxygen gas than when high purity oxygen gas was used alone.

**Electrochemical Methods**

**Patent #3,256,164--June 14, 1966**

**Donohue, John A., et al.** *Electrolytic Production of Ozone.*

In this method of producing ozone, an electric current is passed through a liquid electrolyte, hydrogen fluoride containing not more than 10 weight percent of water, to produce a mixture of gases which contains ozone in large amounts. The procedure is carried out at a temperature of not more than 50°C but preferably between -20°C and +20°C. At least one weight percent of water must be present so that the electric current may pass through the liquid hydrogen fluoride and so that oxygen is present which may be converted to ozone.

**Patent #4,316,782--February 23, 1982**

**Foller, Peter C., et al.** *Electrolytic Process for the Production of Ozone.*

This patent discusses an electrolytic cell for production of ozone with current efficiencies of up to 52%. The cell uses a solution of highly electronegative anions, preferably hexafluoroanions of phosphorus, arsenic, or silicon. The anode is made of either platinum or lead dioxide, and the cathode is made or platinum, nickel, or carbon. A DC current is applied across the electrodes, ozone and oxygen are produced at the anode, and hydrogen gas is produced at the cathode.

**Patent #4,375,395--March 1, 1983**

**Foller, Peter C., et al.** *Process for Producing Ozone.*

This patent describes an electrolytic cell for production of ozone at high current

efficiencies which uses glassy carbon electrodes. The glassy carbon electrodes are highly resistant to corrosion by the fluorine-anion-containing solutions commonly used in electrolytic cells which produce ozone at the anode. The claims are that ozone is produced at high current efficiencies when an electric current is passed through a bare glassy carbon anode and cathode in an electrolytic solution containing highly electronegative $BF_4^-$ or $BF_6^-$ anions. A disadvantage to this method of production of ozone is that glassy carbon electrodes are costly due to the time-consuming method of preparation.

**Patent #4,416,747--November 22, 1983**

**Menth, Anton, et al.** *Process for the Synthetic Production of Ozone by Electrolysis and Use Thereof.*

This patent outlines a process for production of ozone by electrolysis in which the produced ozone is used in water treatment. The anode and cathode are made of stainless steel, and between the anode and cathode is a solid electrolyte made of a plastic polymer based on perfluorinated sulphonic acids. The solid electrolyte serves as a thin ion-exchange membrane which is coated on the cathode side with a layer of a mixture of 85% by weight carbon powder and 15% by weight platinum powder. The anode side of the membrane is coated with $PbO_2$ powder. A solution of oxygen-saturated water is fed into the cell, and ozone is produced in the solution on the anode side of the solid electrolyte ion-exchange membrane while water is formed on the cathode side. The $H^+$ which is produced on the anode side by the decomposition of water to form oxygen and ozone migrates through the ion-exchange membrane and reacts with oxygen

in the water on the cathode side to form water. The evolution of harmful hydrogen at the cathode is thereby suppressed.

**Patent #4,541,989--September 17, 1985**

**Foller, Peter C.** *Process and Device for the Generation of Ozone via the Anodic Oxidation of Water.*

This patent is an outline for an ozone generator using an electrolytic cell. The invention uses an air cathode to reduce the oxygen in air to water, and an inert anode to decompose the water to ozone. This patent claims to provide a method for producing ozone by electrolysis using DC current at levels of ten pounds per day.

**Patent #5,154,895--October 13, 1992**

**Moon, Jae-Duk.** *Ozone Generator in Liquids.*

This patent outlines a method of ozone generation in liquids which can be used in controlling biohazards in food processing, pharmaceutical chemical processing, treatment of water supplies, minor sewage disposal, and in various other disinfection techniques. The proposed ozonizing apparatus consists of one or more pairs of strip electrodes made of an oxidation-resistant metal such as Pt, $PbO_2$, or $SnO_2$ mounted on a substrate inside an ozonizing chamber with outer terminals extending outside the ozonizing chamber. The chamber has an inlet for a liquid such as water or solutions of $H_2SO_4$, $HClO_4$, $HBF_4$, or $H_3PO_4$. An electric current is supplied to the electrodes through the terminals outside the chamber, and water molecules are dissociated at the electrodes producing ozone gas in the liquid. The apparatus

avoids the problems of ozone leakage into the air because it does not use the conventional blower to supply carrier air to the ozone generator.

**Patent #5,203,972--April 20, 1993**

**Shimamune, Takayuki, et al.** *Method for Electrolytic Ozone Generation and Apparatus Therefor.*

This patent is for an electrolytic cell which produces ozone. The electrolyte separating the anode and cathode is a solid electrolyte, preferably a perfluorocarbon sulfonic acid-based ion-exchange membrane. The anode is made by covering a titanium substrate first with a coat of platinum, gold, or like metal, and then with an electrodeposited layer of β-lead dioxide. An electric current is passed through the anode and cathode and ozone is formed at the anode in an ozone resistant anode chamber made of Teflon or titanium.

**Patent #5,332,563--July 26, 1994**

**Chang, Shih-Ger.** *Yellow Phosphorus Process to Convert Toxic Chemicals to Non-Toxic Products.*

This patent outlines a process which involves passing air or oxygen over aqueous emulsions of yellow phosphorus, $P_4$, which results in the formation of $P_4O_{10}$ or $P_20_5$, and an abundance of reactive species such as atomic oxygen and ozone (see Figure 5 at top of next page). The produced ozone is then used to treat solutions containing toxic inorganic or organic compounds by destroying the toxicity of the inorganic or organic components and resulting in a non-toxic solution. This process is a continuation of Patent #5,106,601, April 21, 1992. Patent #5,106,601 outlines a method for removing acid-forming gases such as NO and $NO_2$ from

exhaust gases. Ozone is produced in the process. The method involves passing the exhaust gas which contains oxygen as well as the nitrogen oxides over an aqueous emulsion of yellow phosphorus, $P_4$. The yellow phosphorus reacts with the oxygen in the exhaust gases to form $P_4O_{10}$ or $P_20_5$. The $P_4O_{10}$ then reacts with water vapor or water droplets to form phosphoric acid. When the pH of the emulsion or suspension is 3 or greater, the emulsion absorbs nitrogen oxides. When the phosphorus combines with oxygen molecules to form $P_4O_{10}$ or $P_20_5$, a large amount of atomic oxygen is detected in area of the reaction. The atomic oxygen combines with oxygen molecules to form ozone in the presence of another molecule which remains unchanged after the reaction. The ozone produced oxidizes NO to $NO_2$ which is more easily absorbed by the aqueous emulsion of yellow phosphorous.

**Patent #5,460,705--October 24, 1995**

**Murphy, Oliver J., et al.** *Method and Apparatus for Electrochemical Production of Ozone.*

This patent is for an electrochemical method and apparatus for production of ozone. The apparatus consists of an anode made up of a substrate and a catalyst coating. The substrate is made of either porous titanium, titanium suboxides, platinum, tungsten, tantalum, hafnium, niobium, or similar material, and the catalyst coating is selected from lead dioxide, platinum-tungsten alloys, glassy carbon or platinum. The cathode is a gas diffusion cathode consisting of a polytetrafluoroethylene-bonded, semi-hydrophobic catalyst layer supported by a hydrophobic gas diffusion layer. The catalyst layer consists of a proton exchange polymer, polytetrafluoroethylene polymer, and a metal such as platinum, palladium, gold, iridium, or nickel. The anode and cathode are separated by an ion-conducting electrolyte which is a proton

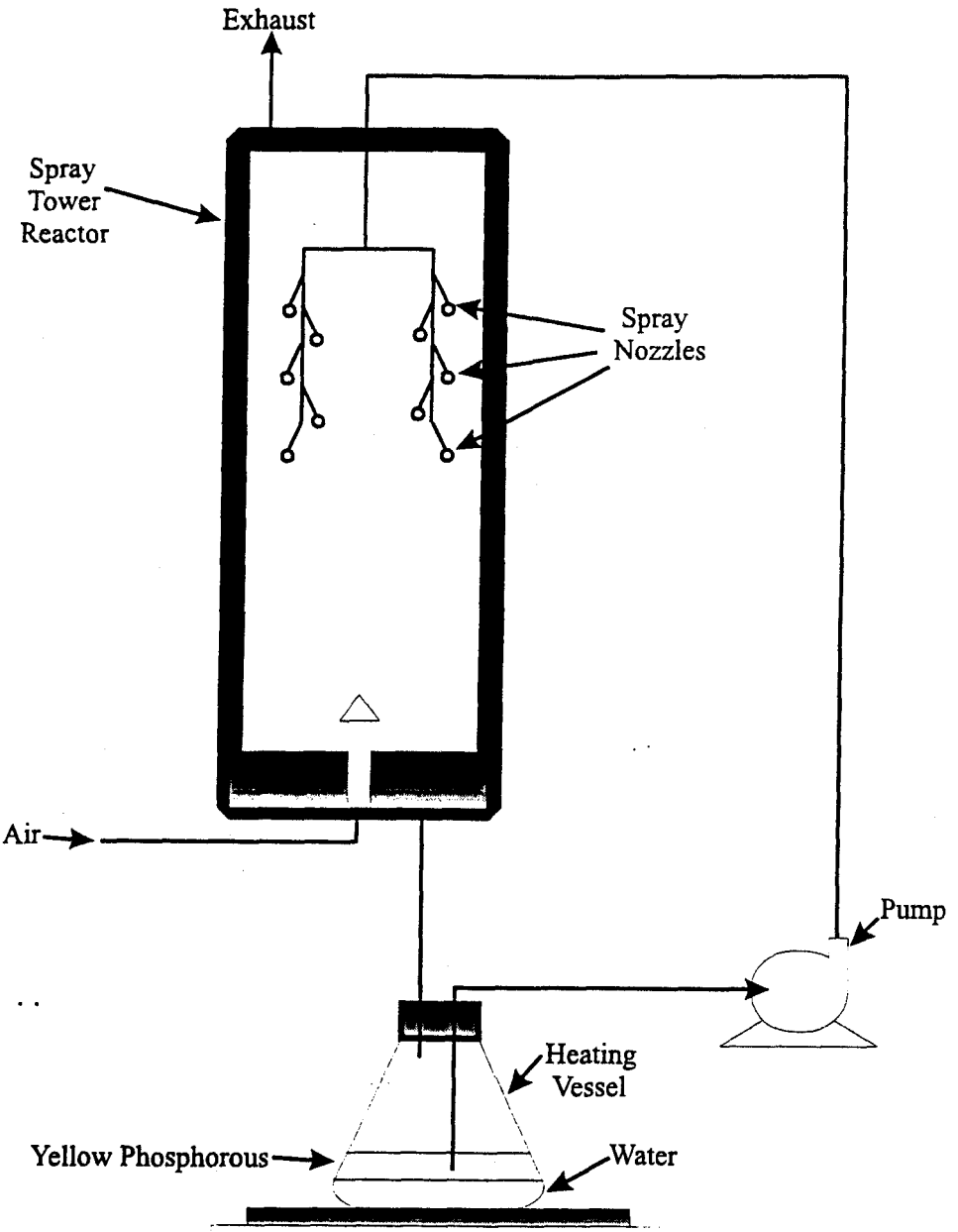


Figure 6: Diagram of Apparatus Detailed in US Patent #5,332,563

exchange membrane with one side bonded to the catalyst layer of the gas diffusion cathode and a second side touching the anode. An electric current is passed through the anode and the gas diffusion cathode, and ozone is formed at the anode.

**Methods Involving UV radiation, laser light, electron beams, etc.**

**Patent #2,937,983--May 24, 1960**

**Ryan, Edmund J.** *Apparatus and Method for Producin a Controlled Ozone Content in Oxygen.*

This patent is for a method of producing a controlled ozone and polymeric oxygen content in purified oxygen gas. The gas containing ozone is then used for therapeutic purposes. In this method, 98% oxygen gas is passed through two columns, one containing fragments of soda lime and one containing active charcoal, in order to remove impurities such as moisture and carbon dioxide as well as solid impurities such as dust particles. This purification process produces oxygen gas of approximately 99% purity. The purified oxygen gas than passes through a reaction chamber containing several coiled quartz tubes filled with inert gases such as argon and krypton. Each quartz tube has electrical lead wires attached to both ends, and the lead wires are surrounded by a globule of mercury in the tube end to improve electrical conductivity between the interior of the quartz tube and the lead wire. Each lead wire is connected to a transformer which supplies a voltage in the range of 3 kV to 10 kV. The electrically energized quartz tubes emit ultraviolet light in the wavelength range of 2,485 Å to 2,537 Å which converts oxygen to ozone and polymeric oxygen. This wavelength range is optimum for destroying bacteria as well as for producing ozone and polymeric oxygen. Each quartz tube is independently electrically energized so that controlled amounts of ozone and polymeric oxygen may be produced. Also, the pressure of the oxygen gas passing through the reaction chamber may be varied to produce differing concentrations of ozone and polymeric oxygen.

**Patent #3,883,413--May 13, 1975**

**Douglas-Hamilton, Diarmaid H.** *Ozone Generator Using Pulsed Electron Beam and Decaying Electric Field.*

This patent describes a system for producing ozone which involves subjecting oxygen in a controlled electric field to a beam of high energy electrons emitted by an electron gun. Oxygen gas is passed through a chamber in which an electric field is created by a sustainer capacitor which is charged by a high voltage supply. An electron beam gun irradiates the oxygen in this chamber with brief bursts of high energy electrons. The oxygen molecules in the chamber dissociate, and the atoms join with oxygen molecules to form ozone. The resulting mixture of oxygen and ozone exits the device through an outlet. The invention is based on the fact that ozone is generated more efficiently when the ratio of current carried by electrons relative to the current carried by ions in the gas is increased. The brief bursts of electrons produced by the electron beam gun increases the electron:ion density ratio, and the efficiency of ozone generation is increased.

**Patent #4,124,467--November 7, 1978**

**Pincon, Andrew J.** *Method and Apparatus for Producing Ozone.*

This patent discusses an ozonizer which uses varying wavelengths of ultraviolet light energy to bombard oxygen gas or air producing varying concentrations of ozone. The apparatus consists of a cylindrical casing coated on the inside with aluminum which is resistant to corrosion by ozone and reflects the ultraviolet radiation back through the gas. The casing has an inlet through which air or pure oxygen gas is fed and an outlet through which the produced ozone

exits the apparatus. Inside the cylindrical casing are six ultraviolet lamps which are equally spaced in a circle. The lamps are made of fluorite glass through which UV light readily passes and are filled with deuterium. The cylindrical apparatus is closed on each ends by caps. The wiring necessary for operating the UV lamps is housed inside the caps. An electrical arc formed between electrodes located inside the end caps and passing through the deuterium-filled tubes will produce UV energy having a wavelength of about 1000 Å, the wavelength at which optimum ozone production is achieved.

**Patent #4,131,528--December 26, 1978**

**Tsujimoto, Minoru, et al.** *Process for the Mass Production of Ozone.*

This patent describes a process for the mass production of ozone. In this process, liquefied oxygen is sent to an adsorption tower containing silica gel, alumina, or some other adsorbent, where hydrocarbons are adsorbed from the liquid oxygen. Next, the liquid oxygen, now free of hydrocarbons, is sent to a heat exchanger where it exchanges heat with air or any suitable fluid such as water. This heat exchange causes the liquid oxygen to become gasified. The gaseous oxygen is warmed between the boiling point of ozone, -112 °C, and the boiling point of oxygen which is -183 °C. The warmed oxygen gas is then sent to a reaction chamber where it is exposed to radiation such as laser beams, electron beams, or plasma radiation. This radiation causes the oxygen gas to be converted to ozone which is in the liquid state at the temperature inside the reaction chamber. The liquid ozone is then pumped from the reaction chamber and collected. The unreacted oxygen gas is then fed back to the heat exchanger, and the process is repeated. The patent also discusses an alternative method of converting oxygen to

ozone in the reaction chamber. This method involves exposing the oxygen gas to an electric discharge instead of exposing it to the ozonizing radiations discussed above.

**Patent #4,182,663--January 3, 1980**

**Vaseen, Vesper A.** *Converting Oxygen to Ozone by U.V. Radiation of a Halogen Saturated Hydrocarbon Liquid Containing Dissolved or Absorbed Oxygen.*

This patent outlines a method for producing ozone dissolved in an inert liquid. Oxygen is absorbed by an inert, dielectric liquid which is non-miscible with water. Pressures in excess of atmospheric pressure are used so that greater amounts of oxygen may be dissolved in the dielectric liquid. The liquid in which oxygen is dissolved is then passed through ultraviolet radiation. The UV radiation energizes the oxygen and converts it to ozone in the liquid. The inert liquid in which ozone is dissolved may then be mixed with waste water for treatment purposes. The liquid, which is non-miscible with water is then easily separated from the water.

**Patent #4,189,363--February 19, 1980**

**Beitzel, Stuart S.** *Process of Producing Ozone in Water.*

This patent summarizes a process for producing ozone in water in order to purify the water. The ozonizing chamber consists of a cylindrical lamp which emits ultraviolet radiation surrounded by a cylindrical chamber into which a mixture of water and air is fed through an inlet. The chamber is separated from the lamp by a cylindrical tube which transmits the radiation emitted by the lamp. The chamber has on the wall facing the lamp a coating of polished stainless steel or a similar material which reflects the radiation from the lamp. The ultraviolet radiation

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# Index by Inventor's Name

passes through the water/air mixture and excites the oxygen to ozone. The chamber also has an outlet through which the treated water exits.

**Patent #4,252,623--February 24, 1981**

**Vaseen, Vesper A.** *Ozone Production Via Laser-Light Energy.*

This patent discusses ozone production using laser light energy which excites oxygen to ozone (see Figure 6). The method consists of passing laser light energy through a stream of oxygen molecules and atoms. The oxygen may be in the gaseous form or may be dissolved in an inert, fully halogenated, dielectric liquid hydrocarbon. The ozone generated from gaseous oxygen may be used immediately, and the ozone which is dissolved in the hydrocarbon may be used up to three days later. With sufficient laser energy, the method may yield up to 99.9% ozone, but the ozone decomposes rapidly due to the heat generated by the laser beam. The inert liquid hydrocarbon absorbs some of the heat, and this method of ozone production is therefore more power efficient.

**Patent #4,317,044--February 23, 1982**

**Vaseen, Vesper A.** *Ozone Production Apparatus.*

This patent describes an ozonizing apparatus which utilizes ultraviolet light energy in the wavelength range of 1100Å to 2200Å at subatmospheric pressures. Oxygen is dissolved in an inert, dielectric liquid such as a fully halogenated hydrocarbon, and the oxygen-rich liquid is then passed through the influent manifold of the apparatus. The dielectric liquid passes through a chamber which houses ultraviolet light sources in the form of elongated tubes. The chamber is

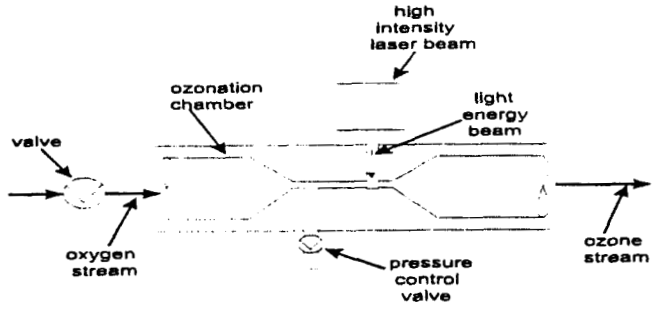


Figure 7: Diagram of Apparatus Outlined in US Patent #4,252,623

surrounded by ultraviolet transparent glass which is coated with an ultraviolet reflective surface. The ultraviolet radiation converts oxygen to ozone, and the dielectric liquid in which 10% of the dissolved oxygen is now ozone, exits the apparatus through the effluent manifold.

**Patent #4,329,212--May 11, 1982**

**Obenshain, David N.** *Method for Making Ozone.*

The method for ozone production described in this patent involves using cathode rays produced by cathode ray tubes to bombard a substance which emits ultraviolet radiation only in the range of 130 to 170 nm (see Figure 7). The substance which emits the radiation is a specially designed phosphor made from a zinc oxide/magnesium oxide matrix with a small amount of an activator added. The range of 130 to 170 nm is optimum for ozone production since UV light in

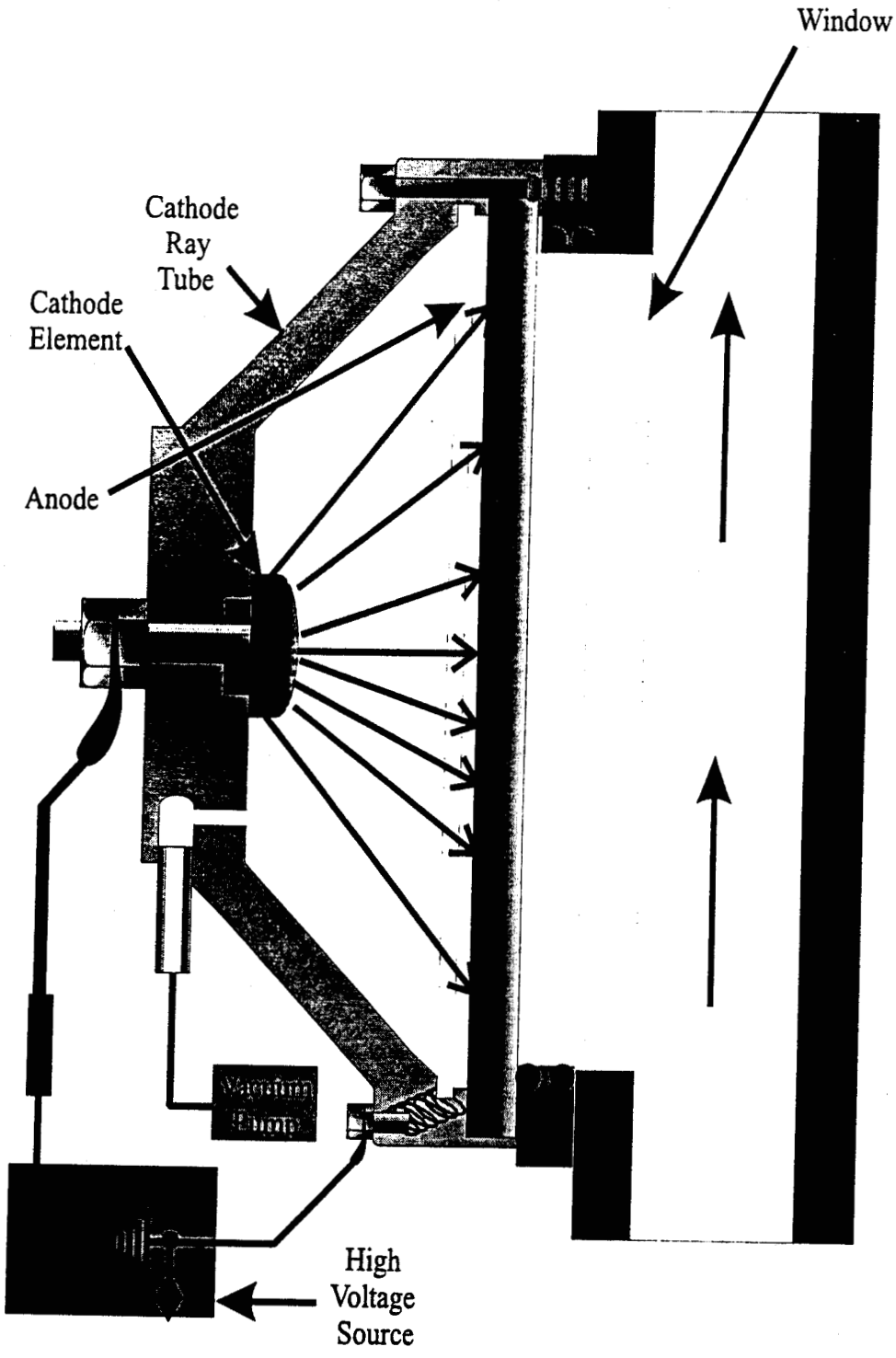


Figure 8: Schematic Diagram of Apparatus in US Patent #4,329,212

this range of wavelengths efficiently converts oxygen to ozone and does not destroy it. Air or oxygen is passed through a duct into a chamber through which the produced UV light is transmitted. The UV light converts oxygen into ozone inside the chamber.

**Patent #4,427,636--January 24, 1984**

**Obenshain, David N.** *Method and Apparatus for Making Ozone.*

This patent details a method for production of ozone that involves exposing oxygen or air to ultraviolet radiation of wavelengths between 130 nm and 170 nm. The UV radiation splits the oxygen molecules into two oxygen atoms which are very reactive and immediately recombine with oxygen molecules to form ozone. Wavelengths outside this range tend to destroy ozone, and the chosen range of wavelengths, 130 nm to 170 nm, is optimum for ozone production. The ozone generating cell in this invention is a cathode ray tube (CRT). The CRT consists of a nonconducting housing inside which is a cathode and an anode. The cathode is convex, and spreads the cathode rays (negative electrons) over a large area. The CRT is connected to a high voltage source and a vacuum pump. Opposite the cathode is a window made of a material such as fluorite that transmits radiation in the desired UV range. The inside of the window is coated with a phosphor prepared from a zinc oxide/magnesium oxide matrix containing an activator which emits radiation only in the optimum range when exposed to cathode rays from the cathode. The window is adjacent to a duct through which oxygen or air is passed; the oxygen or air is bombarded by the UV radiation produced by the apparatus, and ozone is produced.

**Patent #4,857,277--August 15, 1989**

**Broomfield, Paul A.** *Ozone Generating Device.*

This apparatus discussed in this patent is for an ultraviolet ozone generator. The device consists of a tube inside which is located an ultraviolet lamp of the cold cathode light-tube type. An input air duct formed of a ninety-degree ell is attached to the tube which houses the ultraviolet lamp. A fan at one end of the tube draws ambient air into the device, and the air is directed into the light chamber where it is exposed to wavelengths of ultraviolet which optimally convert the oxygen in air to ozone. The ozone is collected from another ninety-degree ell duct at the opposite end of the tube.

**Patent #4,859,429--August 22, 1989**

**Nisenson, Jules.** *Ozone Generating Device.*

This patent details an ozone generator which consists of an elongated cylinder with a fine wire approximately 0.003 inches in the center of the wire and spanning the length of the cylinder. Air to be ionized is fed into the cylinder, and a discharge between the wire and the cylinder results in the conversion of oxygen in the air to ozone. The air serves as a dielectric separating the wire, the inner electrode, and the cylindrical tube, the outer electrode. Air is introduced into the tube in a pulsed manner so that it is exposed to the corona discharge for a longer period of time than in ozone generators in which air is continuously fed into the generator. Continuously fed air pushes ozonized air out of the discharge gap, and the time of exposure to the discharge is less than the time of exposure to the discharge in this generator in which air is pulsed.

**Patent #5,223,105--June 29, 1993**

**Arthurson, Craig J.** *Ozone Generator.*

This patent outlines an apparatus which produces ozone using ultraviolet radiation and a high voltage, low current discharge. An oxygen-containing gas flows through a tube in which it is bombarded by ultraviolet radiation at the same time as it is exposed to a high voltage, low current discharge. This discharge is applied between widely spaced electrodes so that essentially no ozone is produced by the discharge alone. This method of combining UV radiation with a high voltage, low current electrical discharge produces up to ten times more ozone than UV radiation alone.

**Patent #5,387,400--February 7, 1995**

**Pelster, Dennis E.** *Apparatus and Method for Water Purification Using Ozone Generated by UV Radiation with a Continuous Filament Bulb.*

This method involves subjecting an oxygen-containing gas to ultraviolet light radiation of appropriate wavelength in order to convert it to ozone (see diagram at top of next page). The resulting ozone is injected into water in order to destroy undesirable contaminants such as viruses, bacteria, and other organic and inorganic compounds.

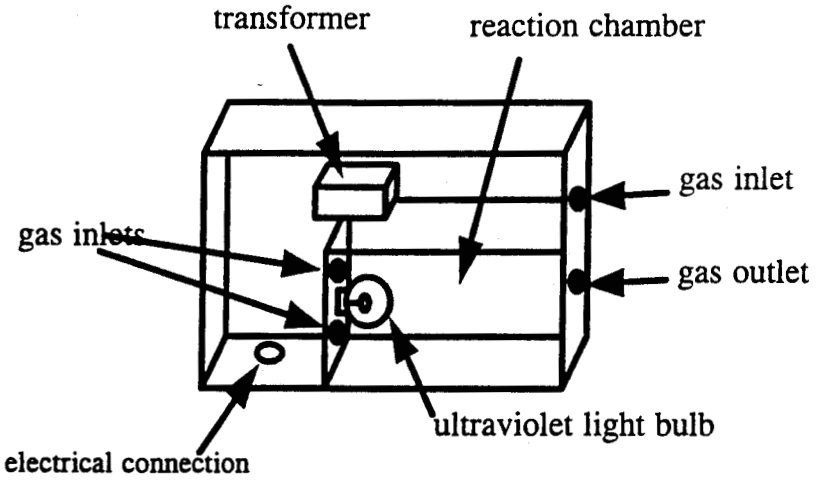


Figure 9: Diagram of Apparatus Detailed in US Patent #5,387,400

## Other Methods

Patent #3,309,300--March 14, 1967

**Grosse, Aristid V., et al.** *Method for the Production of Ozone Using a Plasma Jet.*

This patent is an outline of a method of producing ozone using a plasma jet. A coaxial jet-electrode plasma generator with an inert carrier gas input is used to generate an arc discharge and plasma. A power source which has an output of 0 to 80 volts at 0 to 750 amperes is connected across the electrodes of the plasma generator, and an arc is initiated by a high frequency starter in the power source. The carrier gas may be argon or helium and is used to carry the generated plasma past an oxygen feed inlet which introduces oxygen into the area of the arc and into the path of the plasma. Another feed ring introduces liquid oxygen into the apparatus. The liquid oxygen evaporates and partially dissociates due to the heat produced by the arc, and the dissociated atoms either recombine to form oxygen or react with oxygen molecules to form ozone. The excess liquid oxygen carries the produces ozone to a recovery system where the ozone is separated from the liquid oxygen by a process such as absorption by silica gel. The excess liquid oxygen also serves to quench the arc.

Patent #3,326,747--June 20, 1967

**Ryan, Joseph, et al.** *Disinfecting Solution and Method.*

This patent is for a process for disinfecting water such as swimming pool water and for disinfecting solutions which may be topically applied for disinfecting body surfaces or may be injected parenterally as medication. The process involves ozonizing aqueous solutions of iodine

salts in order to convert the iodide to free elemental iodine and oxides of iodine. This free iodine and its oxides disinfects by destroying bacterial contamination. Ozone is produced in this method by an electrical discharge ozone generator or by an ozone generator which utilizes ultraviolet light.

**Patent #4,095,115--June 13, 1978**

**Orr, Jr., F. D., et al.** *Ozone Generating Apparatus and Method.*

This patent describes a method for producing ozone by exposing oxygen gas at subatmospheric pressure to an electron beam generated by a hollow cathode plasma discharge device (HAD). A chamber containing oxygen at subatmospheric pressure is separated from the HAD by a window of foil made of aluminum, titanium, beryllium, or other suitable metal which transmits electrons. The oxygen gas inside the subatmospheric pressure chamber is moved past the transmissive window at velocities of about 4000 feet per minute, and an electron beam from the HAD converts the oxygen to ozone.

**Patent #4,167, 466--September 11, 1979**

**Orr, Jr., F. D., et al.** *Ozone Generation Apparatus and Method.*

This patent is a continuation of Patent #4,095,115. The ozone generating apparatus is essentially identical to the apparatus described in the previous patent. The method is more defined because a diffuse electron beam is used having a DC level electron energy between 100 and 180 kilovolts. Also, the electron beam generated by the hollow cathode plasma discharge device is generated in pulses.

**Patent #4,167,484--September 11, 1979**

**Morikawa, Masahiro.** *Ozone Generating Apparatus.*

This patent is a method for drying air that is sent to a "conventional ozonizing apparatus." It is claimed that the outlined method for producing the dry air significantly reduces the amount of energy that is generally used in drying the air that is sent to an ozonizer. To this purpose, the ozonizer uses a plurality of adsorbent towers that can be filled with a number of water removing desiccants. Air is pumped through a series of connections to the adsorbent towers and then to the ozone generator. The advantage of the outlined method over other methods that use desiccants to dry air entering into an ozonizer is that the outlined method has a descant recovery step. After air is pumped through the ozonizing chamber, the dry air/ozone mixture is pumped back through the desiccators by using a series of electromagnetic switches to change the direction of gas flow.

**Patent #4,434,771--March 6, 1984**

**Slomnicki, Israel.** *Ozone Production System.*

This patent outlines a process for using ozone in the combustion of hydrocarbon fuels associated with internal combustion engines. The purpose of the design is to increase the efficiency of hydrocarbon combustion by adding ozone as an oxidizing agent in the air stream supplied to the carburetor and to thereby eliminate certain byproducts of hydrocarbon combustion such as carbon monoxide. To eliminate the problem associated with the production of excess ozone, a UV ozone detection apparatus is attached to the exhaust system to monitor ozone emissions. At predetermined levels of ozone in the exhaust, signals are sent to a control apparatus which decreases the electricity supplied to the ozonizer.

Patent #4,786,489--November 22, 1988

**Grenier, Maurice.** *Ozone-Producing Process.*

This patent outlines a process for producing the large quantities of ozone needed at an industrial level. The process begins with the distillation of air to oxygen. The oxygen is then cycled into an ozonizer to produce a 3% by mass ozone/oxygen mixture. The ozone/oxygen mixture is then cycled into a silica column where ozone is adsorbed. The remaining oxygen is recycled into the ozonizer. A secondary effluent stream desorbs the ozone from the silica. The secondary stream is then carried into a scavenging column that removes most of the carrier gas from the effluent.

Patent #4,863,497--September 5, 1989

**Grenier, Maurice, et al.** *Ozone-Producing Plant.*

This patent is for an ozone-producing plant which incorporates several ozonizing loops connected to cylinders filled with silica gel. Each ozonizing loop consists of a compressor, an ozonizer, and a heat exchanger which cools the oxygen-ozone mixture. The produced ozonized air passes through the cylinders filled with silica gel, and the ozone is adsorbed by the silica gel. The remaining oxygen is recycled into the ozonizer, and a substitution gas such as impure nitrogen gas is passed over the column to desorb the ozone from the silica gel.

Patent #5,039,314--August 13, 1991

**Lehner, Franz J., et al.** *Method for Producing Oxygen and/or Ozone.*

This patent outlines a method for producing oxygen or ozone for use in pulp bleaching. The method involves using highly purified oxygen gas which is purified by a pressure-swing adsorption system. The pressure-swing adsorption system separates oxygen from other gases to yield high purity oxygen gas. This high purity oxygen gas is then sent through an ozonizer, and the ozone generated is sent to a bleaching facility. The remaining oxygen is recirculated to the pressure-swing adsorber for further purification, and the process is repeated.

Patent #5,366,703--November 22, 1994

**Liechti, Pierre A., et al.** *Methods and Systems for Forming Process Gases Having High Effective Ozone Content utilizing Isothermal Compression.*

This patent is for a method of producing ozone that uses an isothermal compression step for the purpose of forming a high pressure process gas. In the method that is outlined in this patent, an oxygen containing gas is cooled to a temperature that is no greater than 5ØC. The gas is then fed into a discharge type ozonator and the ozone containing gas that is produced is isothermally compressed to form an industrial process gas with a high partial pressure of ozone. The patent contains several different designs for ozone producing apparatuses that use the previously described process. Furthermore, the purpose of this process is to prevent the fast decomposition of ozone to oxygen that occurs at temperatures greater than 5ØC.

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