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# *FINAL REPORT*

to

## *TIP* [3]

**State of Georgia**

## *ECONOMICAL PRODUCTION OF OZONE FROM AN ELECTRICAL DISCHARGE*

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# INTRODUCTION

Ozone has numerous applications including treating wastewater and in the bleaching process of paper. It is considered an environmental friendly alternative to current methods but is limited by the expense required to produce the strong oxidizing agent. Ozone ($O_3$) can be produced from oxygen ($O_2$) by several methods including an electrical discharge, electrochemical cell an ultraviolet light. Only electrical discharges are sold commercially. The basic aim of this research was to lower the cost of producing ozone for the pulp and paper industry.

This project was funded for two years. The first year was spent building and optimizing an inductively coupled plasma for the production of ozone. An ICP uses a magnetic field to generate a discharge. In addition to building the system at VSU, we ran a range of tests designed to test the novel systems ability to produce ozone. In summary, we encountered two negative trends:

a. We could not go above the 6-8 % conversion efficiency range for any tests. For pure oxygen, this number was in the 1-2% range. This might be considered average and therefore not particularly competitive because it involves new instrumentation.

b. The second problem we encountered was the power cost. It was in the 30 kW/kG/hr - also not a competitive rate.

From the work with the 27.12 MHZ ICP we learned two important things:

a. We had the highest efficiencies in argon-oxygen plasmas.

b. We could operate argon-oxygen plasmas with less power than a pure oxygen discharge.

From this work we shifted our emphasis from the ICP, an attempt at using a new type of instrument to produce ozone, to using the inert gases as catalysts in a discharge with a high field erntstrenght (67,000 V/cm), simple electrodes (stainless steel), in a economical container (PVC).

This report centers on the three major aspects of the projects:

**a. Patent application (Draft) - this describes in detail how the system works.**
**b. Signed confidentiality agreements from four sources.**
**c. Search we completed to confirm that our idea is unique and patentable.**

In summary we can report that the system we developed is economically competitive considering instrumentation cost, conversion efficiency, and power consumption. The patent application is being handled by the firm Carnes, Cona, and Dixon (Tallahassee, Fl.).

draft

**TITLE OF INVENTION: Discharge Process For The Production Of Ozone Incorporating Mixed Gases In a Self Contained Loop**

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## ABSTRACT

The catalytic use of inert gases is demonstrated to increase the efficiency and economy of producing ozone ($O_3$) from high purity oxygen in a process incorporating an electrical discharge. The inert gases are used economically due to incorporation in a self contained loop. Using an argon-oxygen mixture, the system produces ozone at an efficiency of 9.5% and a power cost of 5.43 Kw/Kg/hr.

## BACKGROUND OF THE INVENTION

1. Field of Invention

This application relates to a new method for the production of ozone. Specifically, it concerns the economic production of gases containing ozone from gases including oxygen, helium, argon, and neon. Helium, neon, and argon, individuality or mixed, act as catalysts in the production of ozone.

2. Description of the Prior Art

Ozone ($O_3$) is made from the stable molecular oxygen ($O_2$). Ozone is unstable and decomposes slowly (minutes) at ambient temperatures and rapidly (< 1 sec) at higher temperatures. Because of this instability, it must be manufactured on-site for industrial applications. Current technology in ozone production is carried out by several techniques. One approach utilizes electrochemical techniques and includes U.S. Patent #5,332,563; #4,316,782; #4,375,395, #4,135,995, #5,460,705, #5,407,550. These systems suffer from high electrical consumption. The cells produce chemicals that can be toxic or difficult to dispose. For example, #5,407,550 (*Electrode Structure for Ozone Production and Process for Producing the Same*) uses an electrochemical cell to produce ozone. The system uses a perfluorocarbon sulfonic acid-based ion-exchange membrane as the electrolyte. Because electrochemical cells involve an anode and cathode conducting electricity *through a solution or a solid*, they can be evaluated as a completely different type of ozone generator than that proposed here.

The second general approach utilizes electrical discharges and include U.S. Patents #5,569,437, #4,131,528, #5,366,703, #5,223,105, #4,417,966, #5,098,671, #5,124,132,

#5,370,846, #4,863,701, and 5,518,698 These systems, which pass either pure oxygen or air in the gas phase through an electric field generated by putting a voltage between an anode and a cathode, suffer from high electrical consumption and a low conversion efficiency from oxygen to ozone. None of these inventions demonstrate the ability to increase the oxygen to ozone efficiency using inert gases. Patent #5,370,846 (*Apparatus and Method for Generating High Concentration Ozone*) outlined a novel silent discharge and tested it will several gases including argon and helium. In #5,370,846 the efficiency demonstrated for inert gas (Ar, Ne, He)-oxygen mixtures in their generator are less then a nitrogen-oxygen mix. The efficiencies measured here for the inert gas-oxygen mixtures are greater than the nitrogen-oxygen mixture. The discharge used in #5,370,846 showed a decrease in ozone production for the argon-oxygen and helium oxygen mixture as a function of time indicating a change in discharge conditions. They offered no explanation for this anomaly. This data would indicate an instrumentation fault, perhaps electrodes overheating. Our data remained constant with time using a corona discharge. We were able to use the inert gases to significantly increase the efficiency of production and offered a viable theoretical model/process to explain the results. #5,370,846 only uses gas mixtures for argon and helium in the 1-10% range while this data shows that the greatest gains are made in higher percentage ranges.

In patent #5,518,698, it was demonstrated that the efficiency of oxygen to ozone generation can be improved in an electrical discharge introducing the oxygen at an angle. The inventors were able to show a power cost per kilogram of ozone of 5.9 Kw/Kg/hr at 8% efficiency using their invention. This invention, although a completely different approach, demonstrates a power cost efficiency of 9.5 % at 5.43 Kw/Kg/hr under optimum conditions.

There are other inventions using high energy methods such as UV light, beta rays, and lasers to convert the oxygen to ozone but these have found limited large scale commercial application. Patents such as #3,702,973, #5,387,400 are indicative.

The commercial applications of ozone include wastewater treatment (#5,637,231), disinfectant (#5,614,151), fabric cleaner (#5,611,868), chemical etcher (#5,599,740), and beaching agent (#5,658,429).

Like oxygen, chlorine, and hydrogen peroxide, ozone is a strong oxidizing agent.

| | | |
|---|---|---|
| $O_2 + 4H_3O^+ + 4e^- \rightarrow 6H_2O$ | $E^o = +1.23$ V | (1) |
| $Cl_2 + 2e^- \rightarrow 2Cl^-$ | $E^o = +1.36$ V | (2) |
| $HClO + H_3O^+ + e^- \rightarrow 2H_2O + 1/2Cl_2(g)$ | $E^o = +1.63$ V | (3) |
| $HClO_2 + 2H_3O^+ + 2e^- \rightarrow HClO + 2H_2O$ | $E^o = +1.63$ V | (4) |
| $H_2O_2 + 2H_3O^+ + 2e^- \rightarrow 4H_2O$ | $E^o = +1.77$ V | (5) |
| **$O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O$** | **$E^o = +2.07$ V** | **(6)** |
| $F_2 + 2e^- \rightarrow 2F^-$ | $E^o = +2.87$ V | (7) |

Ozone has some well known advantages over other strong oxidizing agents. For example, $HClO_2$ and HClO leave behind a chlorine based residue and fluorine gas ($F_2$) is highly corrosive.

Current applications of ozone are limited by the cost of instrumentation related to ozone generation, the consumption of electricity, and the low efficiency of converting oxygen to ozone. The present invention demonstrates a process that uses a self contained recirculating loop that makes the use of an inert gases economical. The inert gases allow ozone to be synthesized from oxygen more efficiently. In particular the present invention concerns the utilization of an electrical discharge system to generate oxygen atoms and oxygen molecules that combine to form ozone in an inert gas stream. The present invention uses inert gas and oxygen mixtures in a self contained loop to efficiently and economically to significantly improve the conversion efficiency of oxygen to ozone. The present invention utilizes the ability of the inert gases to control of the plasmas temperature, electron density, the average ionization potential of the high purity oxygen and inert gas mixture, and the fundamental thermodynamic parameters important in ozone production using an electrical discharge systems.

**OBJECTS**

A principal object of the invention is the provision of a new method for the economical production of ozone incorporating inert gases in an electrical discharge.

Further objects include the provision of:

1. New catalyst for ozone production
2. Ozone containing process gases have specific inert gas (Ar, Ne, He)
3. The inert gases consist of oxygen and 1 or more inert gases at specific ratios.
4. The process gases are utilized in a self contained loop.

Other objects and additional scope of applicability of the present invention will become apparent from the detailed description given herein. It should be understood that the detailed drawings and descriptions are given as a way of illustration only since changes and modifications within the spirit and scope of the invention will become apparent from such descriptions.

A process for generating ozone, comprising the steps of (a) utilizing an electrical discharge system with an inert gas and oxygen mixture, (b) transporting the gas mixture to an application chamber where the ozone is utilized © the gas mixture, once bubbled through the reaction chamber, is removed of unwanted vapor by chemical desorption and low temperature (d) these gases are then repressurized, (e) the ratio of inert gas or gases is held maintained at a constant ratio (f) and returned to the discharge. It is demonstrated that inert gases, in conjunction with oxygen, can be used to increase ozone efficiency in an electrical discharge system and that inert gases can be used economically if a recirculating loop is incorporated. The inert gases also lower the power consumption of the discharge.

The foregoing has outlined some of the more pertinent objects of the invention. These objects should be construed to be illustrative of some of the more prominent features and applications of the intended invention. Many other positive results can be obtained by applying the disclosed invention in a different manner or modifying the invention within the scope of the disclosure. Accordingly, a fuller understanding of the invention may be had by referring to the detailed description in addition to the scope of the invention defined by the claims taken in conjunction with the accompanying drawings.

**Brief Description of the Drawings**

**FIG 1** is a diagrammatic illustration that outlines the process for producing ozone. The plasma/electrical discharge unit converts oxygen to ozone and the spectrometer quantifies it. The application vessel represents the range of applications possible for ozone. Once sent through the reaction chamber, the inert gas, oxygen, ozone gas has its temperature lowered to remove unwanted vapors. The oxygen/inert gas mixture is repressurized, combined with gases from the cylinder to maintain a constant ratio of inert gas or gases to oxygen and back through the discharge unit.

**FIG 2.** is a diagrammatic illustration of the ozone application chamber.

**Figure 3**. The output of ozone with argon, helium, and oxygen is demonstrated to be constant with time.

**Figure 4**. The decomposition rate of ozone back to oxygen in argon, helium, and oxygen environments are measured to be approximately the same.

**Detailed Description Of The Preferred Embodiment**

FIG 1 shows the ozone generating process. The present invention relates to a process for the efficient production of ozone using a electrical discharge to generate oxygen atoms that recombine with oxygen molecules to form ozone. The method comprises of the inert gas or gases (1) and oxygen (2) stored in pressurized cylinders and introduced into the process at a process not to exceed 50 °C. The $O_2$ and inert gas flow rate are controlled by valves (3). The inert gas acts as a catalyst in the conversion of oxygen to ozone. The electrical discharge **(4)** is characterized by converting the gas mixture to relatively high temperatures, electron densities, and ion densities. The system produces an oxygen/inert gas discharge that produces ozone. The discharge power supply (5)draws 110 volt AC. The twelve inch corona discharge tube has stainless steel

electrodes separated by a gap of approximately 1 millimeter and has a voltage of 6700 volts ac across it. The system operates at 60 Hertz.

A ultraviolet spectrometer (**6**) set at 254 nanometers (nm) is used to quantify the ozone levels. This system uses an ultraviolet light source that is focused and collimated through a quartz cell that is in line with the oxygen/inert gas/ozone stream that is being transported from the discharge to the separation chamber. Ozone absorbs light in the ultraviolet, with its maximum absorbance coming at 254 nm. The ultraviolet light source allows for the continuous monitoring of the ozone concentration. The ultraviolet spectrometer is separated from the electrical discharge unit by approximately 10 feet of 1/4 inch tubing.

From the Beers Law relationship:

$$A = \epsilon bc \qquad (8)$$

The absorbance (A) of ozone at 254 nm is proportional to its concentration (c in moles per liter for ozone) and a cell path length (b) in centimeters. $\epsilon$ (3,000 centimeters-liters per mole) is the extinction coefficient for ozone. Other gases used (e.g. He, Ar, Ne, $O_2$, $N_2$) do not absorb ultraviolet light to any significant degree in this region.

The ozone/oxygen/inert gas mixture is transported to the application vessel (**7**). At this point ozones role as a strong oxidizing agent is utilized. Specifically, the ozone is bubbled through a solution and a fraction of the oxidizing agent dissolves into the liquid. The undissolved bubbles of gas consisting of the inert gas, oxygen, unreacted ozone, and vapor exits above the application vessel.

The gas mixture from the reaction chamber is pulled through a chemical desorption chamber composed of silica gel (9) that removes organic contaminants. The gas mixture is than pulled through a low temperature chamber (**10**) that removes water vapor. The purified inert gas-oxygen mixture is repressurized (**11**) and returned to the discharge (**4**). The amount of oxygen entering the gas stream is adjusted to maintain a constant oxygen/inert gas ratio in the discharge. This loop allows the inert gases to be used economically. All metal fittings are made from stainless steel to minimize corrosion.

FIG 2 is a diagram of the application chamber from FIG 1 (7). The inert gas, oxygen, and ozone mixture enters the chamber **(12)** and is bubbled through the solution (13). A fraction of the ozone dissolves in the aqueous solution. A stir bar **(14)** and stirrer **(15)** are used to insure a homogeneous solution. The inert gas, oxygen, unreacted ozone and vapor exit the application ion chamber through stainless steel tubing **(16)**.

Table 1 is experimental data obtained with this process that demonstrates the effect that inert gases have on the efficiency of ozone production from a electrical discharge. In each comparative case, the total flow and pressure are held constant but the ratio of the gases (He, Ne, Ar, $N_2$) to oxygen is varied. Experiment 1 is a pure oxygen discharge, experiments 2 thru 20 are nitrogen/oxygen, argon/oxygen, neon/oxygen and helium/oxygen mixtures, and experiments 21 through 25 are a summary of the three gas mixture (argon/helium/oxygen) experiments. The argon, neon and helium cause significant gains in the efficiency of ozone production. Nitrogen ($N_2$) affects the efficiency of the ozone formation to a smaller degree than does the argon, neon or helium. In addition to the lower efficiency, nitrogen will cause the formation of various $N_xO_y$ species (where $x,y > 0$), which is undesirable.

**TABLE 1.** Twenty-five experiments summarizing the affects of the inert gases on the production of ozone.

| Exp. # | $O_2$ (l/min) | Ar (l/min) | Ne (l/min) | He (l/min) | $N_2$ (l/min) | Average I.P. (eV) | $O_3$ produced (g's/hr) | Efficiency ($O_3/O_2$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 10 | - | - | - | - | - | 2.18 | 0.25 |
| 2 | 8 | 2 | - | - | - | - | 3.94 | 0.57 |
| 3 | 6 | 4 | - | - | - | - | 6.21 | 1.21 |
| 4 | 4 | 6 | - | - | - | - | 7.61 | 2.22 |
| 5 | 2 | 8 | - | - | - | - | 7.04 | 4.11 |
| 6 | 1 | 9 | - | - | - | - | 8.06 | 9.42 |
| 7 | .05 | 9.95 | - | - | - | - | 0.94 | 22.0 |
| 8 | 9 | - | 1 | - | - | - | 3.31 | 0.43 |
| 9 | 5 | - | 5 | - | - | - | 7.80 | 1.82 |
| 10 | 3 | - | 7 | - | - | - | 7.44 | 2.89 |
| 11 | 9 | - | - | 1 | - | - | 4.22 | 0.55 |
| 12 | 6 | - | - | 4 | - | - | 7.24 | 1.41 |
| 13 | 5 | - | - | 5 | - | - | 6.93 | 1.62 |
| 14 | 2 | - | - | 8 | - | - | 3.52 | 2.05 |
| 15 | 1 | - | - | 9 | - | - | 0.12 | 0.14 |
| 16 | 9 | - | - | - | 1 | - | 2.59 | 0.33 |
| 17 | 7 | - | - | - | 3 | - | 2.25 | 0.37 |
| 18 | 5 | - | - | - | 5 | - | 2.31 | 0.54 |
| 19 | 3 | - | - | - | 7 | - | 2.30 | 0.89 |
| 20 | 1 | - | - | - | 9 | - | 1.74 | 2.04 |
| 21 | 1 | 1 | - | 9 | - | 23.7 | 3.45 | 4.03 |
| 22 | 1 | 3 | - | 7 | - | 21.9 | 4.44 | 5.18 |
| 23 | 1 | 5 | - | 5 | - | 20.2 | 5.68 | 6.63 |
| 24 | 1 | 7 | - | 3 | - | 18.4 | 6.79 | 7.92 |
| 25 | 1 | 9 | - | 1 | - | 16.6 | 8.11 | 9.46 |

Experiment 6, using an argon-oxygen mixture, gives the best combination of efficiency of oxygen to ozone conversion, and quantitative production (grams of ozone per hour) of any experiment. In experiment 7, a 0.5% oxygen (0.05 liter per minute) and 99.5% argon (9.95 liters per minute) mixture resulted in an efficiency of oxygen to ozone conversion greater than 22% but this resulted in less than 1 gram of ozone per hour. Because argon is 0.9% of the atmosphere, it is the most economical of the inert gases to use.

The data in Table one and two should be construe as typical results. Experimental details such as: gas flow rates, gas pressure, gas purity, gas inlet temperature, electrical voltage and frequency, electrode geometry, the average dielectric constant of the chemicals between the electrodes, and the electrode coverings are examples of parameters that can be varied easily and effect results such as efficiency, grams per hour, and power required.

The following thermodynamic considerations are considered for optimum design in the efficient and economic production of ozone from oxygen. First, the production of ozone from oxygen is an endothermic reaction:

$$3O_2(g) \rightarrow 2O_3(g) \qquad \Delta H = +286 \text{ kJ/mol} \qquad (9)$$

The discharge provides the energy needed to convert oxygen to ozone. Second, the decomposition of ozone to oxygen is thermodynamically favored:

$$2O_3(g) \rightarrow 3O_2(g) \qquad \Delta G = -326 \text{ kJ/mol} \qquad (10)$$

This decomposition can be slowed by lowering the temperature of the system. The goal of this process is to provide enough energy to convert the oxygen to ozone and to cool the ozone molecules as rapidly as possible. The inert gases rapidly dissipate energy gained in collisions by emitting electromagnetic radiation. If the discharge energy is to low, equation 9, the formation of ozone from oxygen, will not take place. If the discharge energy is not dissipated rapidly, equation 10, the decomposition of ozone, will be accelerated. The inert gases (He, Ne, Ar) are an economical chemical medium that will not react with oxygen or ozone.

The inert gases can be used to test a range of temperatures and electron densities. Helium, with a high ionization potential (IP), will form a relatively cool plasma with a relatively low electron and ion ($He^+$) density. Argon, with a lower ionization potential, will form a relatively hot plasma with a higher electron and ion ($Ar^+$) density. Neon falls between argon and helium.

In experiments 20 through 24, mixing the inert gases allows a specific temperature and electron density range to be selected and tested for various levels of ozone production. For example, a 50% argon (I.P. = 15.76 eV), 50% He (I.P. = 24.58eV) mix will produce a discharge gas with an effective IP of 20.17 eV and a temperature and electron density between that of a pure helium and argon plasma. By mixing these gases in different ratios, the average ionization potentials of the plasma is varied from 15.76 eV to 24.58 eV. This data shows the variation in ozone production as the He/Ar ratio varies and indicates that as there is a lower ionization

potential and subsequentially a higher temperature, ozone production increases.

In this invention, the ozone output is constant with time (see U.S. Patent # 5,370,846). FIG 3 shows the results of three experiments measuring the ozone output by ultraviolet spectrometer (**6**) from the electrical discharge (**4**). The first experiment is operating with a pure oxygen discharge (10 l/min $O_2$), a argon/oxygen mixture (9 l/min Ar, 1 l/min $O_2$), and a helium/oxygen mixture (5 l/min He, 5 l/min $O_2$) over 60 minutes.

The catalysts (i.e. inert gases) do not accelerate decomposition of ozone at ambient temperatures compared to pure oxygen. FIG 4. shows the result of three experiments that measured the decrease of $O_3$ concentration in a sealed quartz container in three carrier gases (Ar, He, and $O_2$). The 10 cm quartz cell in the ultraviolet spectrometer **(6)** was clamped off at each end to measure the decomposition of ozone in a static cell at ambient temperature. The three experiments had the following concentrations of carrier gases: *1.* Ar 90%, $O_2$ 10% *2.* He 40%, $O_2$ 60% *3.* $O_2$ 100%. The first order rate constants (k) for the decomposition of ozone ( $r = k[O_3]^1$)in the three mediums are: -.00445 (±.002) $min^{-1}$, -.00766 (±.002) $min^{-1}$, and -.00556 (±.002) $min^{-1}$, respectively. This data illustrates that the decomposition of ozone in an Ar, He, or $O_2$ medium occur at a similar rate at ambient temperature.

For the economical production of ozone, the power consumption is an important facet to be minimized. The discharge (4) uses electrical power to raise the temperature of the gas mixture significantly. The amount of energy ($\Delta H$, calories) needed to raise a certain mass of gas (m, grams) from ambient temperature to discharge temperatures ($\Delta T$, Kelvin) can be estimated from the following relationship:

$$\Delta H = mc\Delta T \qquad (11)$$

The average specific heat (c) of the gas mixture is lowered by the inert gas. This minimizes the energy ($\Delta H$) required to raise the temperature of the gas discharge to the value needed to maintain a discharge that can efficiently produce ozone. Argons' specific heat (0.124 calories/gram/Kelvin) is approximately half that of molecular nitrogen (.249 calories/grams /Kelvin) and molecular oxygen (.219 calories/grams/Kelvin), making the argon discharge more efficient than an air

discharge or pure oxygen discharge in terms of the electrical power required to raise the gas temperature to discharge conditions. The four different experiments (A, B, C, D) in table 2 demonstrate the lower power cost, higher quantitative yield, and higher efficiency of the argon-oxygen discharge (B) compared to the pure oxygen (A), neon-oxygen (C), and helium-oxygen ( D) discharges. The power includes both the electrical discharge and cooling unit.

Table 2. Comparison of efficiency, power cost, and grams per hour for discharges.

| Parameters | Exp. A Pure $O_2$ | Exp. B $Ar/O_2$ | Exp. C $Ne/O_2$ | Exp. D $He/O_2$ |
|---|---|---|---|---|
| $O_2$ (l/min) | 10 | 1 | 3 | 6 |
| Argon (l/min) | - | 9 | - | - |
| Neon (l/min) | - | - | 7 | - |
| Helium (l/min) | - | - | - | 4 |
| Power (W) | 49 | 44 | 46 | 51 |
| grams per hour | 2.20 | 8.11 | 7.44 | 7.31 |
| Efficiency (%) | 0.25 | 9.5 | 2.89 | 1.48 |
| Power Cost (Kw/Kg/hr) | 22.3 | 5.43 | 6.20 | 6.98 |

In the inert gas/oxygen discharge, there are minimum endothermic reactions in the discharge to compete for energy with the formation of ozone and ionization of the carrier gas. This is particularly important in comparing the oxygen-inert gas discharge to an air discharge. In the argon discharge, only two endothermic reactions are of significance in the formation of ozone:

$$126.5\ \text{kJ/mol} + Ar(g) \rightarrow Ar^{+}(g) + e^{-}(g) \qquad (12)$$

$$286\ \text{kJ/mol} + 3O_2(g) \rightarrow 2O_3(g) \qquad (13)$$

Having only these two reactions (ionization of Ar and $O_3$ formation) is optimum. The argon ion

($Ar^+$) and electron ($e^-$) couple with the electric field generated across the electrodes and deliver the energy (286 kJ/mol) needed to convert oxygen to ozone.

In an air discharge (≈ 80% $N_2$, 16% $O_2$), in addition to the formation of ozone (eq. 13) and the ionization of the carrier gas (eq. 14):

$$125.3 \text{ kJ/mol} + N_2(g) \rightarrow N_2^+(g) + e^-(g) \qquad (14)$$

the reactions outlined below (eq. 15-18) will compete for energy with the processes essential to ozone formation. This increases power consumption in ozone production in an electrical discharge.

$$180.5 \text{ kJ/mol} + N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad (15)$$

$$944 \text{ kJ/mol} + N_2(g) \rightarrow 2N(g) \qquad (16)$$

$$66.4 \text{ kJ/mol} + N_2(g) + O_2(g) \rightarrow 2NO_2(g) \qquad (17)$$

$$164 \text{ kJ/mol} + 2N_2(g) + O_2(g) \rightarrow 2N_2O(g) \qquad (18)$$

The stable products of these reactions (e.g., NO, $NO_2$, etc.) have been found in the products of air fed ozone generators. None of these chemical reactions (eq. 15-18) are needed in the production of ozone from oxygen.

As many apparently different embodiments of this invention can be made without departing from the scope of this invention is not limited to the specific embodiments described but only as defined in the appended claims.

**WE CLAIM:**

1. A method of increasing the quantity of ozone generated by a silent discharge in a high purity oxygen and inert gas mixture comprising:

a. An ozonizing chamber having a material gas inlet and a product gas outlet and ozonizer discharge electrodes in said ozoning chamber

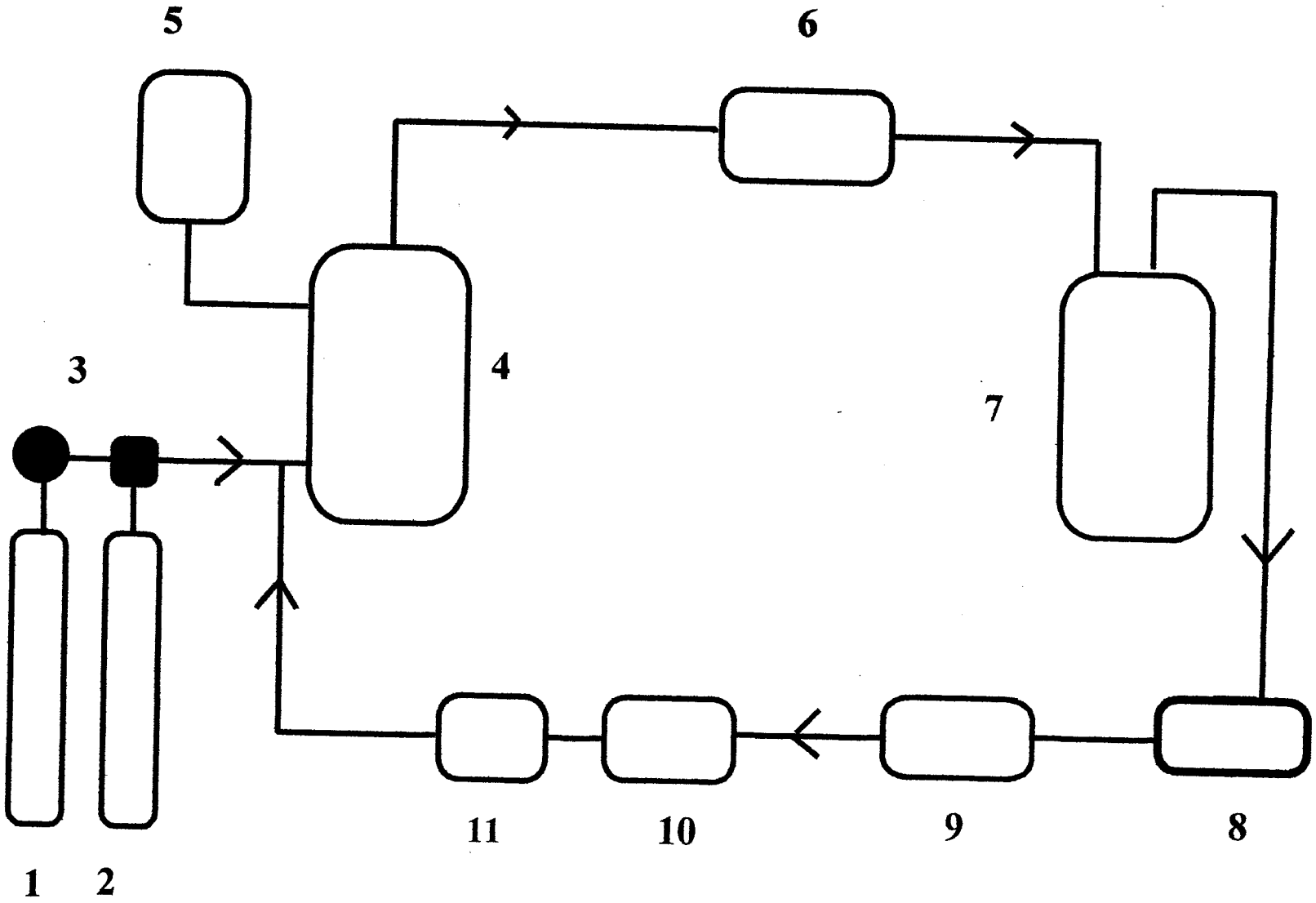
b. A AC high-voltage power supply wherein ozone generating electrodes associated with ozone generating units are connected to said power supply

2. The method in claim 1 including mixing the either helium, neon, or argon or a mixture these inert gases and oxygen before introducing the mixture into the ozone generating apparatus.

3. The method of claim 1 wherein said process gas has an efficiency of oxygen to ozone conversion between 0.55 and 22%.

4. The method in claim 1 where the power cost (Kw/Kg/hr) is minimized by lowering the average specific heat of the gas mixture and minimizing unnecessary endothermic reactions.

5. The method in claim 1 where the inert gases and unconverted oxygen can be used more economically if they are cleansed of unwanted vapor or molecules and recirculated back to the discharge.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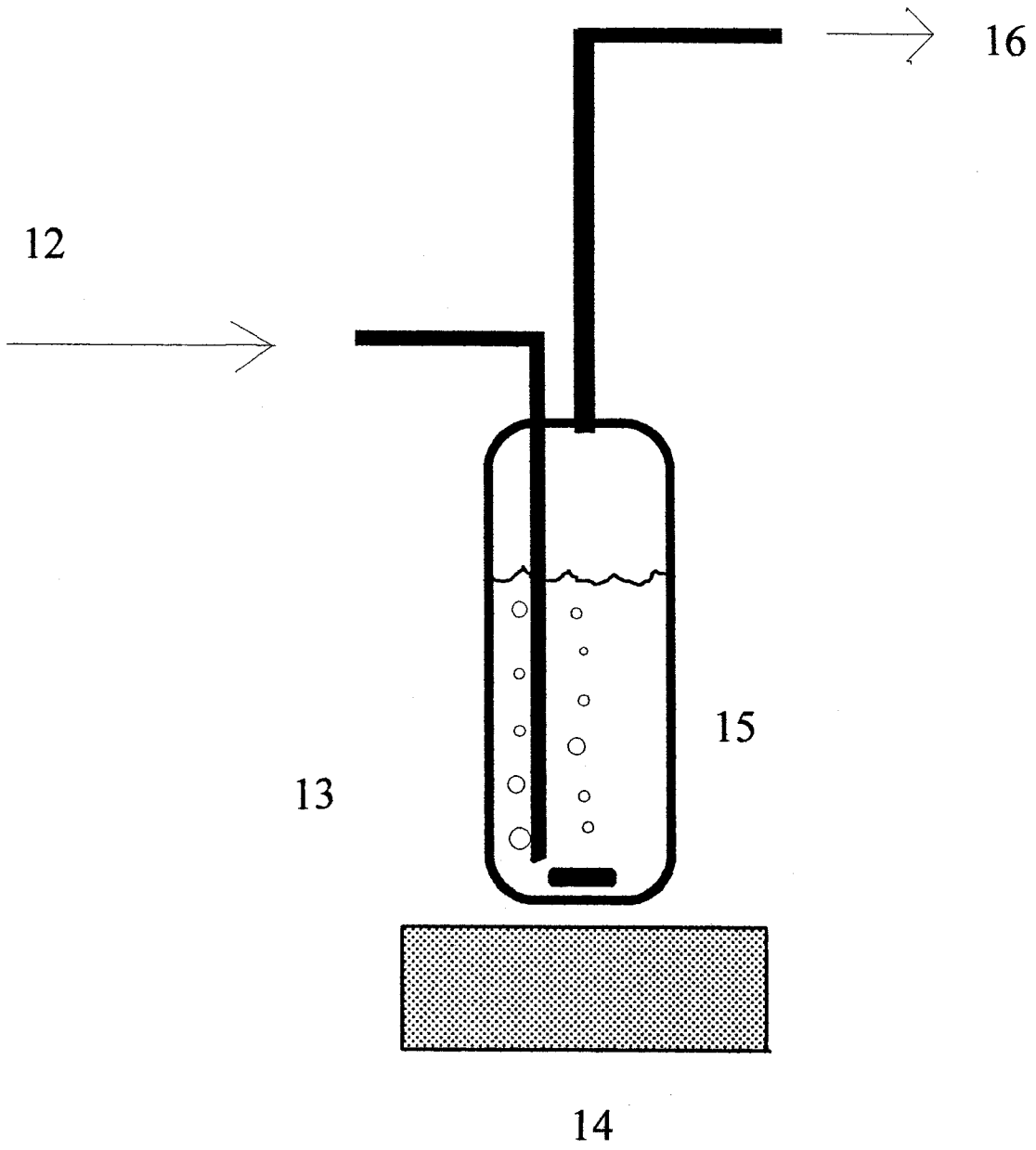
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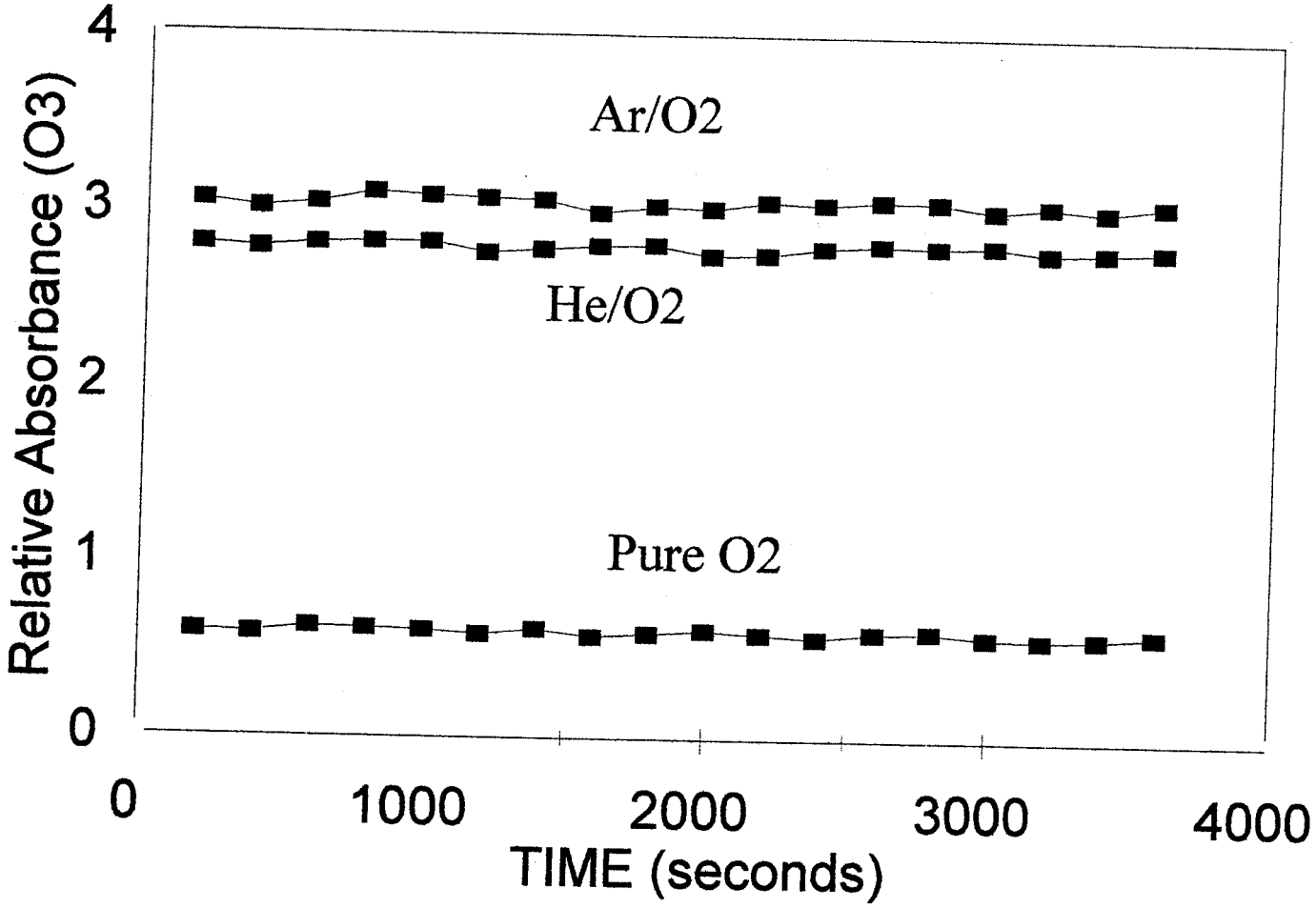
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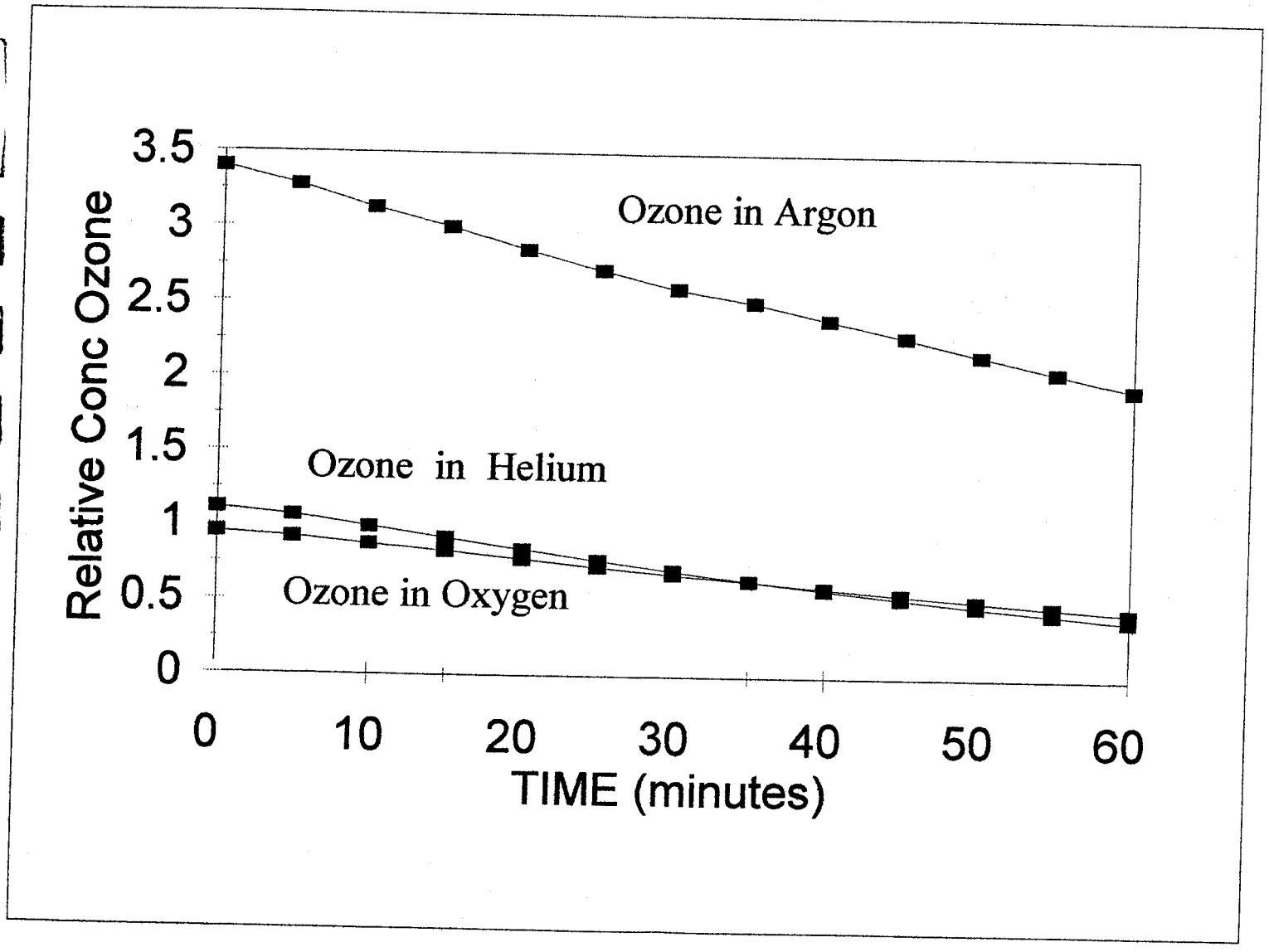
Pure O2
0
1000
2000
3000
4000
TIME (seconds)


Relative Conc Ozone
3.5
3
2.5
2
1.5
1
0.5
0
Ozone in Argon
Ozone in Helium
Ozone in Oxygen
0
10
20
30
40
50
60
TIME (minutes)

FEDEX

PRAXAIR TRAILIGAZ

**Praxair-Trailigaz Ozone Co.**
11501 Goldcoast Drive
Cincinnati, Ohio 45249-1643
513-530-7702
FAX: 513-530-7711

May 9, 1997

Mr. Thomas J. Manning
Chemistry Faculty
Valdosta State University
Department of Chemistry
Valdosta, Georgia 31698-0200

Dear Mr. Manning:

We have received your letter of April 2, 1997 concerning a catalyst that improves ozone generation efficiency. We have interest in learning more about this invention.

Enclosed is the signed confidentiality statement. Note that I have amended the agreement to include our parent company Trailigaz (France) as they will be performing a technical evaluation of the invention.

Please advise if you have any questions. We are looking forward to receiving the initial information.

Very truly yours,

Barry L. Loeb
President

**TRADE SECRET**

**AND**

**CONFIDENTIAL DISCLOSURE AGREEMENT**

**THIS AGREEMENT**, entered into this April 1 day of 1997, by and between Praxair-Trailigaz Ozone Company and Trailigaz Compagnie Générale de l'Ozone (hereinafter referred to as "Recipient"), and Thomas J. Manning (ss# 051-62-9349) of Department of Chemistry, Valdosta State University, Valdosta, Georgia (hereinafter referred to as "Inventor):

**WITNESSETH:**

**WHEREAS**, the inventor has invented a Plasma Process and catalyst for the efficient production of ozone (hereinafter referred to as the "Invention"). This invention is the property of the inventor and he has confidential and trade secret information in his possession relating to the Invention, including supporting disclosure and other written materials relating thereto, and prototypes and/or samples thereof and "know how," all of which is hereinafter referred to as "Confidential Information":

**WHEREAS**, Recipient wishes to review the Confidential Information for the purpose of determining whether or not it is interested in entering into a business relationship with Inventor for manufacturing and/or other trade secret rights from the Inventor which would enable the parties to this agreement to undertake further development and sales embodying the Invention:

**NOW THEREFORE**: In consideration of the premises and covenants herein contained, the parties hereto mutually agree as follows:

1. Inventor shall disclose to Recipient the confidential and trade secret information

regarding the invention.

2. Upon execution of this Agreement, a confidential relationship shall arise between the Inventor and Recipient. The Recipient agrees to hold in strictest confidence all confidential and trade secret information disclosed to it by the Inventor (in writing or other tangible form) and not to disclose such confidential information to anyone except such of its employees as may be necessary and not to use such confidential and trade secret information for such purpose not covered by this Agreement, unless

a. Such confidential and trade secret information is a part of the public domain prior to the date first written hereinabove; or

b. Such confidential and trade secret information becomes a part of the public domain not due to some unauthorized act by or omission of Recipient after this Agreement is executed; or

c. Recipient can demonstrate that it or an affiliate or subsidiary company of Recipient independently developed such confidential and trade secret information; or

d. Such confidential and trade secret information is disclosed to Recipient by a third party who has the right to make such disclosure; or

e. Permission to disclose said confidential and trade secret information or to make use thereof is obtained by Recipient from the Inventor in writing.

3. Recipient shall use such efforts to preserve the confidentiality of the confidential and trade secret information disclosed as it would if the confidential and trade secret information had been developed by the recipient and was to be retained in confidence by it.

4. It is understood and agreed that the confidential and trade secret information referred to hereinafter shall be furnished to the Recipient for evaluation in order that Recipient may determine its interest in entering into a business relationship with the Inventor under an agreement to be negotiated with the Inventor and for no other purposes.

5. If it is determined by either party hereto that an agreement relative to the use of the invention cannot be successfully negotiated, Recipient shall return to Inventor any and all written material and/or prototypes and/or samples furnished by Inventor to Recipient except that Recipient may retain one copy of written confidential and trade secret information in its confidential files for record purposes only. The return of the material shall not affect the obligations of Recipient to treat the confidential and trade secret information disclosed to Recipient as confidential and not to use same, which shall continue for a period of four years from receipt of the information by Recipient.

6. This agreement shall be binding upon and inure to the benefit of the successors and assigns of the parties hereto, but neither of the parties hereto shall assign this Agreement without the prior written consent of the other party.

7. No modification or waiver of any of the provisions of this agreement shall be valid unless in writing and signed by parties hereto.

**IN WITNESS WHEREOF**: The parties have hereunto set their hand the day and year first above written.

By (sign name): Barry L. Loeb Type Name: Barry L. Loeb

Date: May 1, 1997 Title: President

Company: Praxair-Trailigaz Ozone Co City/State: Cincinnati, OH 45249

By (sign name):  Type Name: Alain Delcominette

Date: May 6, 1997 Title: General Manager

Company: Trailigaz Compagnie Général de l'Ozone City/Country: Paris/France

**TRADE SECRET**

**AND**

**CONFIDENTIAL DISCLOSURE AGREEMENT**

**THIS AGREEMENT**, entered into this April 3 day of 1997, by and between _____(hereinafter referred to as "Recipient"), and Thomas J. Manning (ss# 051-62-9349) of _____ Department of Chemistry, Valdosta State University, Valdosta, Georgia (hereinafter referred to as "Inventor):

**WITNESSETH:**

**WHEREAS**, the inventor has invented a Plasma Process and catalyst for the efficient production of ozone (hereinafter referred to as the "Invention"). This invention is the property of the inventor and he has confidential and trade secret information in his possession relating to the Invention, including supporting disclosure and other written materials relating thereto, and prototypes and/or samples thereof and "know how," all of which is hereinafter referred to as "Confidential Information":

**WHEREAS**, Recipient wishes to review the Confidential Information for the purpose of determining whether or not it is interested in entering into a business relationship with Inventor for manufacturing and/or other trade secret rights from the Inventor which would enable the parties to this agreement to undertake further development and sales embodying the Invention:

**NOW THEREFORE**: In consideration of the premises and covenants herein contained, the parties hereto mutually agree as follows:

1. Inventor shall disclose to Recipient the confidential and trade secret information

regarding the invention.

2. Upon execution of this Agreement, a confidential relationship shall arise between the Inventor and Recipient. The Recipient agrees to hold in strictest confidence all confidential and trade secret information disclosed to it by the Inventor (in writing or other tangible form) and not to disclose such confidential information to anyone except such of its employees as may be necessary and not to use such confidential and trade secret information for such purpose not covered by this Agreement, unless

a. Such confidential and trade secret information is a part of the public domain prior to the date first written hereinabove; or

b. Such confidential and trade secret information becomes a part of the public domain not due to some unauthorized act by or omission of Recipient after this Agreement is executed; or

c. Recipient can demonstrate that it or an affiliate or subsidiary company of Recipient independently developed such confidential and trade secret information; or

d. Such confidential and trade secret information is disclosed to Recipient by a third party who has the right to make such disclosure; or

e. Permission to disclose said confidential and trade secret information or to make use thereof is obtained by Recipient from the Inventor in writing.

3. Recipient shall use such efforts to preserve the confidentiality of the confidential and trade secret information disclosed as it would if the confidential and trade secret information had been developed by the recipient and was to be retained in confidence by it.

4. It is understood and agreed that the confidential and trade secret information referred to hereinafter shall be furnished to the Recipient for evaluation in order that Recipient may determine its interest in entering into a business relationship with the Inventor under an agreement to be negotiated with the Inventor and for no other purposes.

5. If it is determined by either party hereto that an agreement relative to the use of the invention cannot be successfully negotiated, Recipient shall return to Inventor any and all written material and/or prototypes and/or samples furnished by Inventor to Recipient except that Recipient may retain one copy of written confidential and trade secret information in its confidential files for record purposes only. The return of the material shall not affect the obligations of Recipient to treat the confidential and trade secret information disclosed to Recipient as confidential and not to use same, which shall continue for a period of four years from receipt of the information by Recipient.

6. This agreement shall be binding upon and inure to the benefit of the successors and assigns of the parties hereto, but neither of the parties hereto shall assign this Agreement without the prior written consent of the other party.

7. No modification or waiver of any of the provisions of this agreement shall be valid unless in writing and signed by parties hereto.

**IN WITNESS WHEREOF**: The parties have hereunto set their hand the day and year first above written.

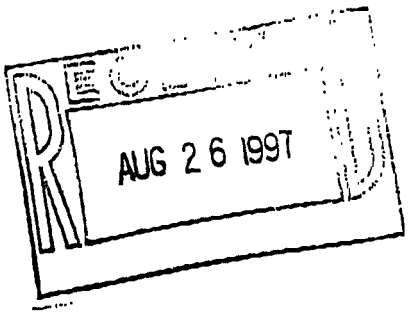
By (sign name): _____ Type Name: J. Stach

Date: 4/7/97 Title: CEO

Company: BF Power Prod. City/State: Voorhees, NJ

OZONIA® NORTH AMERICA

2924 Emerywood Parkway
Richmond, Virginia 23294
P. O. Box 70145
Richmond, Virginia 23255-0145
Telephone: (804) 756-0500
Telefax: (804) 756-0519




August 25, 1997

VALDOSTA STATE UNIVERSITY
Grants and Contracts
Attn: Mary H. Watson, Ph.D.
Director
Valdosta, GA 31698-0429

re: Valdosta State University letter dated August 12, 1997

Dear Dr. Watson:

Please find attached a signed original "Confidential Disclosure Agreements" with the change initialed as requested.

If you have any questions or comments, please do not hesitate to call my office.

Sincerely,

Richard D. Pingel
Senior Contract Administrator

# CONFIDENTIAL DISCLOSURE AGREEMENT

**THIS AGREEMENT**, entered into this July 22nd day of 1997, by and between Ozonia North America (hereinafter referred to as "Recipient"), and Valdosta State University, Valdosta, Georgia (hereinafter referred to as "Inventor"):

**WITNESSETH:**

**WHEREAS**, the Inventor has invented a "Plasma Process and Catalyst for the Efficient Production of Ozone" (hereinafter referred to as the "Invention"). This Invention is the property of the Inventor, and he has confidential information in his possession relating to the Invention, including supporting disclosure and other written materials relating thereto, and prototypes and/or samples thereof and "know how", all of which is hereinafter referred to as "Confidential Information":

**WHEREAS**, Recipient wishes to review the Confidential Information for the purpose of determining whether or not it is interested in entering into a business relationship with Inventor for manufacturing and/or other trade which would enable the parties to this agreement to undertake further development and sales embodying the Invention:

**NOW THEREFORE**, in consideration of the premises and covenants herein contained, the parties hereto mutually agree as follows:

1. Inventor shall disclose to Recipient the Confidential Information regarding the Invention.

2. Upon execution of this Agreement, a confidential relationship shall arise between the Inventor and Recipient. The Recipient agrees to hold in strictest confidence all Confidential Information disclosed to it by the Inventor (in writing or other tangible form) and not to disclose such Confidential Information to anyone except such of its employees as may be necessary and not to use such Confidential Information for such purpose not covered by this Agreement unless:

   a. Such Confidential Information is a part of the public domain prior to the date first written hereinabove; or

   b. Such Confidential Information becomes a part of the public domain not due to some unauthorized act by or omission of Recipient after this Agreement is executed; or

c. Recipient can demonstrate that it or an affiliate or subsidiary company of Recipient independently developed such Confidential Information; or

d. Such Confidential Information is disclosed to Recipient by a third party who has the right to make such disclosure; or

e. Permission to disclose said Confidential Information or to make use thereof is obtained by Recipient from the Inventor in writing.

3. Recipient shall use such efforts to preserve the confidentiality of the Confidential Information disclosed as it would if the Confidential Information had been developed by the Recipient and was to be retained in confidence by it.

4. It is understood and agreed that the Confidential Information referred to hereinafter shall be furnished to the Recipient for evaluation in order that Recipient may determine its interest in entering into a business relationship with the Inventor under an agreement to be negotiated with the Inventor and for no other purposes.

5. If it is determined by either party hereto that an agreement relative to the use of the Invention cannot be successfully negotiated, Recipient shall return to Inventor any and all written material and/or prototypes and/or samples furnished by Inventor to Recipient except that Recipient may retain one copy of all Confidential Information in its confidential files for record purposes only. The return of the material shall not affect the obligations of Recipient to treat the Confidential Information disclosed to Recipient as confidential and not to use same, which shall continue for a period of four years from receipt of the information by Recipient.

6. This agreement shall be binding upon and inure to the benefit of the successors and assigns of the parties hereto, but neither of the parties hereto shall assign this Agreement without the prior written consent of the other party.

7. No modification or waiver of any of the provisions of this agreement shall be valid unless in writing and signed by both parties hereto.

8. Any dispute or claim arising out of or relating to this agreement, or any breach thereof, shall be settled by arbitration administered by the American Arbitration Association under its Commercial Arbitration Rules, and judgment on the award rendered by the arbitrator(s) may be entered in any court having jurisdiction thereof.

9. ~~Virginia~~ Georgia law shall govern the rights and obligations of the parties.

**IN WITNESS WHEREOF:** The parties have hereunto set their hand the day and year first above written.

Valdosta State University

By: Thomas Manning
Name: Thomas Manning
Title: Associate Professor

Ozonia North America

By: Joseph M. Giannone
President
7/22/97

By. Dr. Mary H Watson
Director Grants & Contracts
Valdosta State University

Dated: 8/12/97