Ultraviolet/Activated Oxygen
A New Air Pollution Control Technology Comes of Age

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Introduction

During the last five years, an innovative new approach to air pollution control equipment has been developed through the cooperative efforts of engineers from Terr-Aqua Enviro Systems (TAES), General Dynamics, San Diego County Air Pollution Control District (SDAPCD), and South Coast (L.A.) Air Quality Management District (SCAQMD). Utilizing the photocatalytic effects of tuned frequency ultraviolet light on volatile/reactive organic compounds in combination with "activated oxygen" oxidizers, including ozone and peroxides, emission control systems have been developed with capture and destruction efficiencies in the 95% to 99% range. Depending on the contaminants involved and the sources such as spray booths, ovens, mixing rooms, coating processes, etc., the specific system designs include aqueous phase scrubbing and activated carbon adsorption. Oxidant generated on-site, as required, it utilized to neutralize captured organics on a continuing basis. The resultant air exhaust stream contains the harmless by-products carbon dioxide and water.

Extensive testing under SDAPCD and SCAQMD jurisdiction, utilizing EPA and California Air Resources Board guidelines, has proven this new technology to be "Best Available Control Technology." The system installed at the Pomona, Naval Weapons Development Laboratories for General Dynamics received the First Annual Clean Air Award for Innovative Technology from SCAQMD. TAES UV/AO Systems have been on line and operational for up to five years, treating a broad range of organic compounds.

No one technology nor a single black box can solve all our environmental problems, but each successful new technique becomes a step toward the goal of environmentally friendly and safe industrial activities. The UV-Oxidation technology is now one of these steps and we can truly say, "A New Air Pollution Control Technology Has Come of Age."

History/Background of UV/AO Technology

In 1985 the General Dynamics, Electronics Division in San Diego, California determined that the various metal parts coatings utilized in their spray painting operations could not be successfully reformulated to meet San Diego County Air Pollution District (SDAPCD) regulations for Volatile or Reactive Organic Compounds (VOCs). SDAPCD has adopted rules requiring substantially reduced reactive hydrocarbons in industrial coatings including military specification compounds. These regulations provided for the use of alternative measures such as control equipment for achieving the required emissions reduction instead of "compliant coatings." General Dynamics (GD) Environmental Management personnel investigated available control equipment and technology for VOCs without finding anything
to meet their Corporate goals of "Zero Discharge" and no "Regulated By-products". The Terr-Aqua Enviro Systems technical group approached GD with a proposal to utilize their newly developed Ultraviolet Light and Activated Oxygen/Oxidant Technology for controlling the VOC emissions at the San Diego facility. After reviewing the proposal a contract was entered into for the development, fabrication and installation of this first of its kind UV/AO Air Pollution Control System.

The basic idea for utilizing UV and Activated Oxygen or Ozone for Air Pollution Control came from nature. The studies of smog producing mechanisms and the data on Earth's stratospheric ozone layer being destroyed by very stable organic compounds like chlorofluorocarbons (CFC's) demonstrated very clearly the potential for controlling and neutralizing emissions of numerous organic compounds if these processes could be accomplished inside a system with complete safety, containment and high efficiency. In essence, this technology utilizes UV, plus ozone and other oxygen based oxidants (UV/AO) to create smog and complete the process of oxidation. Some of the specific equipment designs and process techniques are proprietary and the subject of patent applications.

The first UV/AO Air Pollution Control System was installed, tested and given a permit to operate at GD San Diego in 1986. The success of this System lead to a second installation utilizing an aqueous phase at the Pomona, California Naval Weapons Development Laboratories operated by GD. Then, a third System was designed into the original construction of a 400,000 square foot production facility for the GD Air Defense Systems Division in Rancho Cucamonga, California. This System utilizes the UV/AO Technology to control various Toxic Emissions in addition to VOCs.

Activated Oxygen/Ozone

Activated Oxygen is a family of oxygen based oxidants, mainly ozone, with peroxydes, OH, O-, and other radicals which are highly active. Ozone in the lower atmosphere is a major constituent of smog. In the stratosphere it protects the earth from excess UV radiation and in various industrial applications, it is a strong oxidizing agent. Ozone is an almost colorless blue gas with a pungent characteristic odor. The name Ozone is derived for the Greek work Ozin which means "to Smell". This odor characteristic of Ozone may account for its excellent safety record in use, as it is easily detected by humans at low part per million levels, making leak detection very simple.

Ozone (O₃) is a triatomic allotrope of oxygen and is one of the strongest commonly available commercial oxidizing agents. The use of ozone and peroxydes for purification, disinfection, detoxification, deodorization and other industrial oxidation processes is well known and accepted. The high redox potential, or oxidizing power, of ozone allows it to react rapidly with a large variety of organic and other compounds. Ozone can be produced commercially by two specific methods; spark gap or corona discharge generation and Ultraviolet Light of the appropriate frequency. With either method, the generation of ozone must be accomplished at the site of usage. This is due to the relatively short ozone half-life at ambient or higher temperatures. Terr-Aqua utilizes a specific Ultraviolet frequency in conjunction with a catalyst to produce Activated Oxygen/Ozone as required by the air.
pollution being treated in a system. This approach can use clean dry air as the feed gas for the photochemical reaction without producing undesirable Nitrous Oxides (NO₂). The Activated Oxygen species are all excellent oxidizers. In fact, these compounds are 10 to 12 percent more reactive than an equivalent amount of straight ozone, as measured by the oxidation of iodine to iodine, the official EPA test for ozone. The main benefit of the AO species is that many environmental applications require a high redox potential and kinetic energy to break chemical bonds.

_Ultraviolet Light_

The photocatalytic effects of ultraviolet light on various organic compounds and most particularly Volatile forms has been of great interest to the scientific community in recent years. In this new Pollution Control Technology, the "natural" reactions observed in the smog forming process and the stratospheric ozone layer destruction by CFCs and other more stable organics, have been utilized to neutralize VOCs, toxics and other organics in industrial exhaust streams. Key factors such as UV intensity and exposure time have been addressed by the design of full scale systems. A major problem faced during the development phase of UV/AO technology was scale up from test and pilot size systems to full scale equipment capable of handling 5,000, 10,000 or even a 100,000 SCFM of contaminated air streams on a 24 hour per day, 365 days per year basis. For the purposes of these systems the transmission of energy by UV can be considered instantaneous, but this does not solve the question of intensity and duration of exposure required for efficient utilization of the photocatalytic effects on organic compounds in an air stream. A good example of the problem is the difference between Benzene and Chlorodifluoromethane (refrigerant 22). The double bond of a Benzene ring is readily excited and broken by the appropriate UV frequency. Chlorofluorocarbons, on the other hand, are very stable and required high intensity exposure to UV in the presence of oxidants to break down at all.

By means of numerous experiments, various UV frequency ranges have been tested with different organic compounds to determine the most efficient UV tubes for VOCs and Toxic contaminants. This testing showed that a specific UV frequency range is more effective on one class of organic compounds than another. The result is a "tuned frequency" approach to the design of the "Terr-Aqua Photolytic Reactor" through which the exhaust air stream flows for UV exposure and the Photocatalytic effect.

The majority of VOCs and Toxic molecules are only excited by the tuned frequency UV and made more readily oxidizable. This response can be compared to microwaving the organic molecules as the air stream is not significantly heated. Most of the UV energy is transferred to the organic molecules directly exposed, making this a very energy efficient process.

_Carbon Adsorption_

Activated carbon adsorption systems have been used to collect or capture and hold VOCs and Toxics in exhaust streams from paint spray booths, ovens, mixing operations, coating equipment and various other contaminated exhaust flows successfully for many years.
Activated carbon is electrically nonpolar, and therefore it is capable of adsorbing organic and inorganic vapors and gases. Adsorption is a physical phenomenon whereby molecules of the contaminants are trapped and held by the internal submicroscopic structure consisting of tiny capillary passages not greatly larger than the size of the molecules that are adsorbed. The activation process is critical to the efficiency of the adsorption. During activation the structure of multiple capillary passages is created by burning out part of the charred substance to form numerous honeycomb-like internal surfaces, which contain a vast amount of surface area to absorb and hold contaminants. One cubic foot of properly activated carbon will contain approximately 200 million square feet of adsorption surface area, allowing the material to hold from 20% to 50% of its own weight in various VOCs.

Typical System Design

Each system design is based on the most detailed information available about the exhaust air streams to be controlled. Particular consideration is given to the sources of the volatile organics, the relative exhaust gas flows and the volatile breakdown of solvents and coatings used in the source processes. The equipment is designed and sized to treat the maximum required air flows for proper capture of contaminants and to insure capture and complete neutralization of the VOCs or Toxics involved. The multistage nature of the system design enables it to treat a broad range of organic compounds, including halogenated and chlorinated forms.

The systems developed for General Dynamics might be considered "Enhanced Activated Carbon Treatment Systems" as the carbon beds are an integral part of each design. A typical system will operate in the following manner:

1. The exhaust stream from each source will be ducted into a gathering duct system leading to a two-stage pre-filter for micron level particulate removal.

2. The air stream is then directed into the "UV/AO Photolytic- Reactor" where the synergistic Ultraviolet Light/Oxidation process occurs, initiating the reduction-oxidation of VOC in the air. This process is similar to that which occurs in nature where ultraviolet light from the sun works in combination with naturally occurring oxidants to oxidize/reduce VOC. The "UV/AO Photolytic-Reactor" utilizes a specially selected ultraviolet light frequency range to greatly enhance or catalyze the oxidation reaction, thereby increasing the effective reduction of VOC. The UV-AO/oxidant flow to this unit is controlled by the System Process Controller (PLC).

3. The VOC carrying air stream is then directed into the "Aqua-Reactor" where it passes through a complex inert media opposed flow water scrubber. The water in this unit is continually processed through a closed loop recycling tank and filtration subsystem where the water is injected with oxidant to maintain its VOC collection and reduction capability. Through this unique water scrubbing/oxidation process, much of the VOC will be captured and ultimately reduced to carbon dioxide, water and some minor amounts of chlorides. This is particularly true for the more water soluble or miscible compounds. Due to the water recycling process and the
downstream coalescer only minimal amounts of makeup water are required to replace evaporative losses as the air is pushed toward 100% relative humidity. All city water used for make-up is pretreated and filtered to minimize the buildup of contaminants from this source. The effluent water contains no VOC and only minor amounts of dissolved solids such as various chlorides. The recycled water quality and the effluent water are constantly monitored by the System Process Controller. A blow-down treatment tank and final water filter ensure that nothing but legal water is sent to the sewer when required for maintenance purposes.

4. Leaving the "Aqua-Reactor", the air stream passes through a coalescer stage of standard design utilizing chemically inert medial for extended trouble free life and efficiency operation in the removal of water vapor from the air.

5. The air stream is then directed to one of two (2) parallel and redundant flow paths through an activated carbon adsorber/reactor chamber. On alternate days, each chamber becomes an operational adsorber while the other chamber is being regenerated by controlled oxidant flow from the UV/AO generators. This generator utilizes ozone and other highly reactive species that reduce the trapped VOC to nontoxic legally exhausted compounds, including carbon dioxide and water. The controlled final effluent exhaust from the chamber in regeneration mode will merge with the inlet of the "UV/AO Photolytic-Reactor" and then flow to the chamber in adsorber mode carrying the full air flow for delivery to ambient atmosphere. The dual redundant carbon adsorber/reactor chambers acts as final clean/pure air filters to ensure 95% or better VOC/Toxic removal with the system operational 24 hours per day, 365 days per year, if required.

6. The treatment air stream will then pass through the regenerative blower used to eliminate pressure drop or air flow reduction throughout the total exhaust treatment system.

7. As the air flow in the final clean exhaust stack goes to atmosphere, it passes a monitor and control sampling point where regular VOC sampling will verify emission levels. In the event of a failure resulting in unacceptable emission levels at the sampling point, the process control system will automatically alert operators for shutdown and appropriate repair or maintenance action. Prior to automatic shutdown, the carbon adsorber chamber in regeneration mode will be brought on line as the operational adsorber in order to continue system operations while maintenance/repair activities are instituted. A caution or early warning level for high VOC emissions may be developed based on experience to allow for remedial action prior to actual failure.

UV-AO Air Pollution Control System Equipment Description

A. Exhaust duct gathering system flange and ducting to and through the UV/AO System  
   - Exterior has a protective seal coating with a chemically inert interior, and is
structurally supported for mounting as required. Stainless steel is used wherever oxidant contact is possible in ducting.

B. Pre-filter - The exterior housing material and coating on the Pre-filter is the same as ducting but with replaceable filter media of chemically inert polypropylene and fiberglass fibers, designed to remove particulate from air flows with a 99% efficiency rating for removal of particles down to 1 micron in size. This filter utilizes a first stage with a 95% efficiency rating for 5 micron particles and a second stage hepa type filter with a 99.7% efficiency rating for 2 micron particles.

C. Photolytic Reactor - The "Photolytic-Reactor" is a proprietary design welded, sealed, stainless steel chamber housing with a UV-AO/oxidant sparing device, special tuned frequency ultraviolet lamps and air stream flow control vanes. This unit is designed to give the air stream with VOC sufficient contact reaction time for efficient excitation/oxidation of the organic molecules.

D. "Aqua-Reactors" - The Aqua-Reactor is made of high quality, chemically stable, filament wound, fiberglass reinforced plastic with corrosion resistant polyester resin materials and are completely sealed from the environment. These specialized scrubbers utilize the counter flow method with water flowing down the media while the air is forced up through and maximize exposure and VOC removal/reduction. The design and materials utilized allow UV-AO/oxidant to be injected into the water for oxidation of the captured VOC. The coalescer outlet is of standard design using chemically inert media for extended trouble-free life and efficient operation in the removal of water vapor from the air stream. To enhance the mass transfer for improved VOC capture, a newly developed high efficiency media is used.

E. Carbon Chambers - The dual activated carbon adsorber/reactor chambers utilize flow through beds containing activated carbon. This carbon is specially produced to specifications for gaseous or vapor phase adsorption with micropores from 100% coconut shell type base material. Each adsorber is designed and sized to remove a minimum of 98% of peak load VOC with a minimum holding capacity of 3 days before regeneration is required. The chamber structure is designed not only to hold the beds but also to maximize the effective diffusion of oxidants, etc. during the regenerative mode. During the regenerative operation, the unit is sealed from the blower air flow by guillotine doors, while the regeneration/desorption controller flows oxidants into the chamber and the pressure control outlet exhaust is activated. The chamber is welded stainless steel sealed for exterior protection and is a chemically inert material for long life with minimal maintenance.

The equipment is designed with an automatically activated fire fighting sprinkler system. Each adsorber/reactor is fitted with two thermal sensors capable of detecting temperature increases above a preset limit and signaling a controller. This controller will activate the fire control system built into each unit while simultaneously shutting off the blower and other equipment. The built-in doors will also be automatically shut to seal the unit. Both a flashing light, easily visible, and an audible alarm will
be automatically or manually set-off in case of a fire/high temperature condition or an emergency shutdown situation.

F. Blower-Standard industrial grade blower rated for continuous duty for air streams containing VOCs. It is coated and sealed for exterior and interior protection. The blower will maintain required air velocity for contaminant capture at the sources and force process air through the pre-filter and finally out of the carbon adsorber/reactor units.

G. UV-AO/Oxidant Generators - UV/AO Generators are proprietary units using specially designed ultraviolet lamps and a reaction chamber with catalyst, all required controls, filters, blowers and hardware to produce ozone and other reactive species directly from filtered air. The reactor units are constructed from high grade materials for extremely long life without deterioration and will require minimal maintenance, and the outer housings are stainless steel.

H. The Process Controller (PLC) and associated electrical gear are housed in a NEMA approved enclosure with appropriate safeguards. A system status and warning light panel are installed in the source areas, in a readily visible location.

An industrial quality Micro processor based programmable logic controller (PLC) is used to monitor and control all operations. This is a highly flexible solid state unit to control sequences and functions. A storage battery is provided for protection of all logic during a power failure, and additional protection is provided from transients by a Power Surge Control Unit.

Associated with the Process Controller is a multi-point annunciator for all critical functions and monitor-control parameters, with a solid state construction and re-flash re-transmission for operator acknowledgement and alarm silencer. Instrumentation, monitor and control functions are critical for any Air Pollution Control System to operate properly on a long term basis. This is particularly true with UV/AO Systems as no operator is required under normal operating conditions and the operations are fully automated to respond to exhaust source requirements. Carbon regeneration and water recycling purification processes are also automatic, making the monitoring functions very important.

Chart and Flow Diagram

The attached flow diagram represents the Navy/General Dynamics System installed in Pomona, California. The chart of "Typical Reactions of Ozone with Organic Compounds" shows some of the VOCs treated at this facility. As can be seen, when these reactions are taken to completion, the result is carbon dioxide, water and oxygen. Halogenated and chlorinated compounds are usually water soluble or miscible to some degree and are captured in the aqueous phase where the chlorine, bromine or fluorine will stay in the water and combine to form salts, etc.
Conclusions

The Terr-Aqua UV/AO System brings together industrial proven technologies: carbon adsorption/scrubbing and ozone/UV catalysis within a system that is safe and relatively simple to operate. Because the carbon regeneration is a self-contained, automated process, personnel exposure is minimized. The dual redundant adsorption chambers add increasing reliability and the UV/AO regeneration process requires no added thermal energy beyond the exothermic oxidation reactions with the captured VOCs/Toxics. Long activated carbon life is also a plus and no hazardous waste is produced with the normal operation of the UV/AO System. As an added benefit of the UV/AO approach, the recycled water will automatically be EPA compliant for BOD, COD, suspended solids and TDs when sewer blow down is required during maintenance functions.

UV/AO Systems have been on-line and continuously operational for five years without requiring carbon replacement or other major repairs. With normal preventative maintenance the installed systems have not experienced a major failure or unscheduled down time of more than a few hours. The reliability of UV/AO Systems has proven to be exceptional. Pollution Control Regulations have been met without impacting production activities. We can truly state that Ultraviolet/Activated Oxygen Systems represent "A New Air Pollution Control Technology That Has Come of Age" today.
TYPICAL REACTIONS OF OZONE WITH ORGANIC COMPOUNDS

**ETHYL ALCOHOL (ETHANOL) - C₂H₅OH**

\[ 2\text{C}_2\text{H}_5\text{O} + 22 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 8\text{CO}_2 + 6\text{H}_2\text{O} + 23 \text{O}_2 \]

**ISOPROPYL ALCOHOL - (CH₃)₂CHOH**

\[ 2\text{C}_3\text{H}_₇\text{O} + 20 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 6\text{CO}_2 + 8\text{H}_2\text{O} + 21 \text{O}_2 \]

**METHYL ETHYL KETONE (MEK) - CH₃COCH₂CH₃**

\[ 2\text{C}_₅\text{H}_₈\text{O} + 24 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 8\text{CO}_2 + 8\text{H}_2\text{O} + 25 \text{O}_2 \]

**BENZENE - C₆H₆**

\[ \text{C}_₆\text{H}_₆ + 15 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 6\text{CO}_2 + 3\text{H}_2\text{O} + 15 \text{O}_2 \]

**METHYL ISOBUTYL KETONE (MIBK) - (CH₃)₂CHCH₂COCH₃**

\[ 2\text{C}_₇\text{H}_{₁₀}\text{O} + 36 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 12\text{CO}_2 + 12\text{H}_2\text{O} + 37 \text{O}_2 \]

**ISOBUTYL ACETATE - C₆H₅OOCCH₃**

\[ \text{C}_₆\text{H}_{₁₂}\text{O}_₂ + 18 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 6\text{CO}_2 + 6\text{H}_2\text{O} + 19 \text{O}_2 \]

**TOLUENE - C₆H₅CH₃**

\[ \text{C}_₇\text{H}_₈ + 18 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 7\text{CO}_2 + 4\text{H}_2\text{O} + 18 \text{O}_2 \]

**XYLENE - C₆H₄(CH₃)₂**

\[ \text{C}_₈\text{H}_{₁₀} + 21 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 8\text{CO}_2 + 5\text{H}_2\text{O} + 21 \text{O}_2 \]

**ETHYL BENZENE - C₆H₅C₂H₅**

\[ \text{C}_₈\text{H}_{₁₀} + 21 \text{O}_3 \xrightarrow{\text{CATALYZED UV}} 8\text{CO}_2 + 5\text{H}_2\text{O} + 21 \text{O}_2 \]
FLOW DIAGRAM

Terr-Aqua Enviro Systems  UV - OXIDATION TREATMENT SYSTEM FOR V.O.C.

FLOW CONTROL VALVE

LEGEND

- AIR STREAM - V.O.C.
- ACTIVATED OXYGEN FLOW.
- WATER FLOW
- FLOW CONTROL VALVE

* PROPRIETARY TECHNOLOGY/DESIGN