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CORONA GENERATED OZONE - IN-HOUSE DESTRUCTION

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ABSTRACT

The effective management of ozone generated during corona discharge treatment has long since been a major concern to the industry. As Health and Safety and Environmental pressures grow, the necessity to contain and destroy ozone close to source intensifies. This paper discusses the dangers of ozone and how it can be successfully prevented from polluting the workplace and the local environmental atmosphere by using a catalytic decomposition unit.

INTRODUCTION

Ozone (O_3) is a highly toxic and corrosive oxidising agent that is a major danger to health. The recommended human exposure limit is 0.1ppm (0.2mg/m^3) but exposure to 50ppm for 30 minutes can be fatal (Table 1). This colourless gas with its distinctively pungent smell is, as we are constantly reminded, a highly protective necessity in the stratosphere. However, ozone in the work place is, by contrast, an unwelcome pollutant.

It occurs naturally in the atmosphere and is produced whenever ultraviolet radiation or electrical discharge occurs, for example at high altitude and when lightning strikes. Background concentrations vary with the seasons, weather conditions, altitude and humidity but normally these concentrations are low enough not to cause concern. However, it is the high concentrations of ozone generated by certain industrial processes either deliberately, as a vital constituent of the process application, or as a by product that do cause concern.

Increasingly throughout the world both Health, Safety and Environmental lobbies have lead to legislative demands that dictate effective ozone management measures. The straight forward and often traditional method of dealing with ozone laden exhaust by venting to atmosphere, is becoming increasingly less acceptable as it adds to the overall atmospheric pollution load and, in fact in certain countries and States, is illegal.

Corona Discharge Treatment for adhesion promotion is one such industrial process that generates pollution levels of ozone and tight control management of the ozone contaminated exhaust gas is required to prevent leakage into the workplace environment.

Analysis of the problem has lead to a technological solution in the form of Ozone Destruct Units that are becoming an increasingly standard supply with corona treatment machinery.

TABLE 1

EFFECTS OF OZONE	
Concentration ppm	Description of Effects
0.003 - 0.01	Threshold of odour perception by average person in clean air.
0.02 - 0.04	Representative average total oxidant concentrations in major US cities in 1964. Approximately 95% of oxidants is ozone.
0.1	**Recommended exposure limit.** Eye, nose and throat irritation often experienced.
0.2 - 0.5	Reduced dark adaptation and alteration of extra-ocular muscle balance occurs after several hours exposure.
0.5	Nausea and headache sometimes occurs. Extended exposure can cause pulmonary oedema and enhance susceptibility to respiratory infections (both bacterial and viral).
1	10 minutes exposure typically reduces desaturation rate of oxyhaemoglobin to 50%.
1 - 2	Chronic exposure (one year for 6 hours per day) at this level has resulted in bronchiolitis and bronchitis in animals. 2 hour exposure can cause headache, chest pain and dryness of respiratory tract and a reported 30% reduction in timed vital capacity of the lung
1.5 - 2	Exposure for 2 hours typically results in cough, substernal pain and excessive sputum.

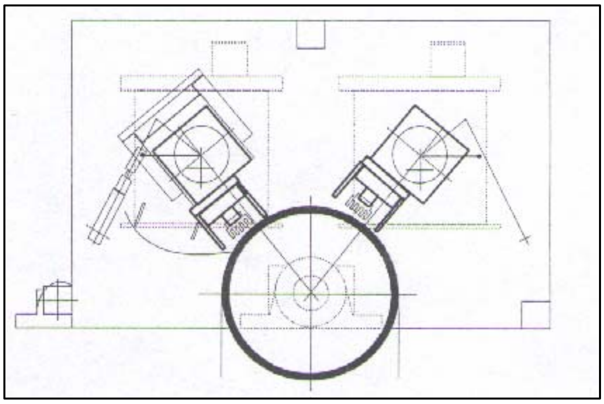
5 - 25	Experimentation showed that 3 hour exposure at 12ppm was lethal for rats and 25ppm was lethal for guinea pigs. Humans (welders) exposed to 9ppm developed pulmonary oedema. Their chest X-rays were normal in 2-3 weeks, but 9 months later they still exhibited fatigue and exertional dyspnoea (Laboured respiration).
50	30 minutes exposure may be fatal.

OZONE GENERATION

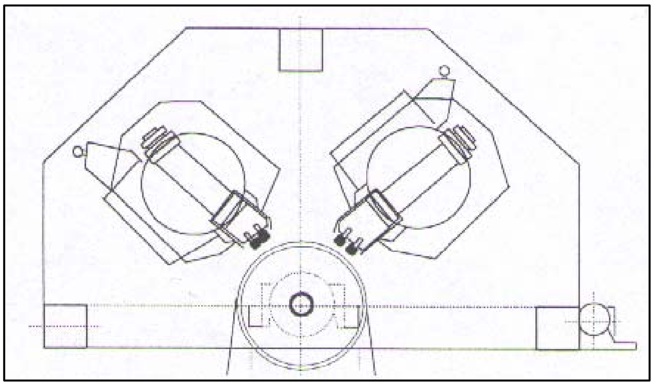
In a corona treater (Diagram 1), the corona is generated by applying a high frequency, high voltage signal to an electrode separated from earth by an air gap and a layer of dielectric material. When a voltage of 3000-5000 V/mm is applied to the electrode, breakdown potential is reached and free electrons are accelerated towards the positive electrode with such energy that they are capable of displacing electrons from molecules in the air gap. The consequence is an avalanche effect, with electrons and the corresponding ions being produced, resulting in current flow across the air gap and thus, the corona effect. It is during this process of electrical discharge that ozone is produced similar to that of a lightning strike.

A - For Non Conductive Substrates
B - For All Material Types

Diagram 1



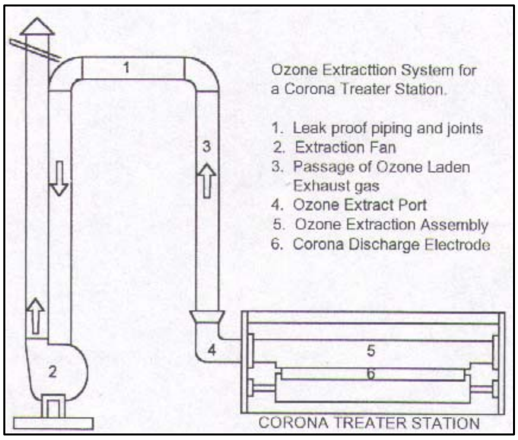
A. For Non Conductive Substrates



B. For All Types of Material

OZONE EXTRACTION

A primary concern in corona treater design has long since been ozone extraction (Diagram 2). For many years electrodes have been enclosed in either fabricated housings or integrated into individual ozone extraction ducts which additionally act to keep the electrodes at an optimum operational temperature. Provided the extraction fans are sized correctly, both types will effectively and efficiently exhaust the ozone contaminated air away from the station. The main criteria for fan size selection are the output power rating of the corona generator, treatment width of the electrodes, substrate line speed, extraction duct configuration and the pressure and flow characteristics of the fan. With this data, a simple computation will determine the correct selection.



Much design effort has also been targeted at achieving leakproof ozone extraction to keep ozone concentration levels around the treater station below the required 0.1 ppm. Given that ozone concentrations in the electrode exhaust are typically in the region 25-30 ppm, which is seriously harmful to man, the demands on the accuracy of the designs are critical in order to keep work station environmental levels below 0.1 ppm. These levels can be monitored locally using a variety of permanent fixtures employing technologies such as chemiluminescence, ultra-violet photometry and electrochemical cells but the use of Draeger vials has proved operationally reliable and convenient and therefore popular.

Corona discharge treaters have had to be designed using components in and around the treater that are corrosion resistant and more specifically ozone resistant. Any exposure of unprotected materials will result in rapid attack and eventual deterioration of the component. This is the case for not only the ducting and extraction fans but also less obvious components like safety interlocks, electrodes assembly bearings and jointing compounds. If insufficient attention is given to this, problems will result.

The traditional extraction system uses ozone resistant ducting coupled to an extract fan, sited within a few metres of the treater station. The ozone laden air gas stream is drawn from the treater station to the fan, after which the gas stream is pushed along ducting to the outside of the building and the ozone is dispersed into the atmosphere.

Any leaks caused, for example, by accidental damage or corrosion, will severely affect the efficiency of the fan because a negative pressure upstream will be created inside the pipe drawing factory air inwards. However, the converse is the case from the fan downstream where there is a positive pressure inside the duct allowing ozone laden air to be leaked from these points into the factory atmosphere and in to the operator area.

Because of this an ozone destruction system is designed to only have a short length of ducting from the treater station and since this is under a negative pressure, any leaks will only allow air to be drawn in with no chance of ozone leakage into the operator area. The system draws ozone by means of a fan, at a temperature higher than ambient air to an ozone destruct unit, so it can gravitate through a layer of catalytic granules, that enable ozone conversion to oxygen.

OZONE DESTRUCTION

Catalytic v's Thermal Incineration

The conventional method of destroying waste gases has been thermal incineration. Oxygen at very high temperatures combines with hydrocarbons to form carbon dioxide and water, and also with carbon monoxide to form carbon dioxide. The use of high temperatures for relatively long periods is the basis of thermal incineration as a method of oxidation.
Catalytic incineration similarly combines with hydrocarbons and carbon monoxide to form harmless end products, but the oxidising reaction occurs at much lower temperatures and consequently with lower energy costs.

Catalytic Ozone Elimination

Over the years of catalyst development two particular types of catalyst have emerged as being most suitable for the conversion of ozone to oxygen (1) Activated Carbon, (2) Manganese Dioxide.

1. *Carbon*

Carbon's main advantages are that it is easy to source and relatively inexpensive, but the chemical reaction between ozone and carbon results in the carbon being consumed and thus exhausting the filter bed during a period of operation.

More importantly, carbon is an absorbent for oil mist vapours and hydrocarbons and in the presence of a strong oxidising agent, such as ozone, hot spots will occur in the centre of the carbon granules. Under these circumstances there is a strong possibility that the localised exotherm will initiate combustion.

There have been reports of carbon absorbent beds setting on fire due to similar reactions and, in hydrocarbon processing technology, carbon is never used as an absorbent. Thus activated carbon filters must under no circumstances be exposed to ozone concentrations higher than 20 g/m^3 (EH38 Guidance Notes).

2. *Manganese Dioxide*

With an inert absorbent such as Manganese Dioxide, hot spots do not represent a hazard as any temperature rise is dissipated.

The inert absorbent is actually a mix of manganese dioxide and copper oxide (MnO_2/CuO) with proprietary promoters to assist the transformation of ozone to oxygen. The material functions through a continuous oxidation-reduction cycle. The manganese is reported as supplying a source of active oxygen for the reaction and accelerates the decomposition of ozone into oxygen without itself undergoing any change in composition. Thus in theory, the expected life of the catalyst is indefinite as it is not consumed in the reaction and is independent of the ozone concentration passing through.

In practice, the catalytic activity deteriorates over time due to contamination of the active sites with materials present in the gas stream other than ozone. Some forms of deactivation are readily controlled, for example particulates will mask the catalytically active surface and cause a reduction in ozone destruction activity.

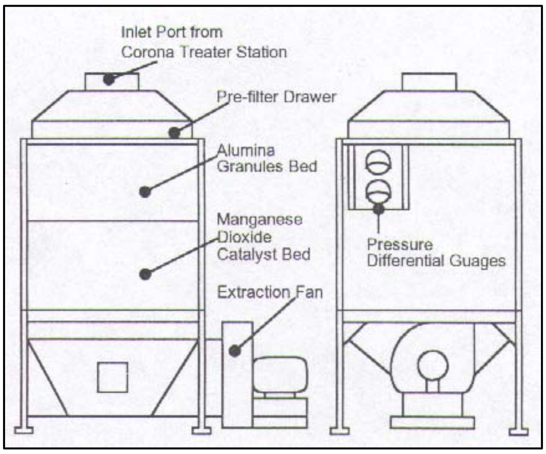
This form of deactivation is controlled by using pre-filters which remove the particulates from the gas stream prior to contact with the main catalyst.

Catalysts function by lowering the active energy requirements for a given chemical transformation, which results in a low capital investment with low operating expenses and maintenance costs. Because of this the catalytic decomposition of ozone is usually preferable to non catalytic alternatives.

THE OZONE DESTRUCT UNIT LOCAL TO THE CORONA TREATER STATION

A general purpose fibre glass filter is fitted in a removable drawer, one filter prior to the catalyst and one filter after the catalyst. The filter is made up of evenly distributed bonded and coated glass fibre mats of constant density faced with scrim and enclosed in rigid frames. The performance of these filters is constantly monitored by differential pressure gauges which indicate when the filters require replacement. The gauges are checked every 4 weeks and, dependent upon contamination in the gas stream, filters are changed as necessary (Diagram 3)

As the manganese dioxide is a microporous chemical it is deactivated by moisture, acidic gases and oils or organic non-volatile compounds which simply sit on the active surface and block the sites of catalytic activity.



These poisoning agents are fairly typical of those found in the gas stream from a corona treating station. In order to avoid their contact with the main catalyst it is necessary to use a secondary pre-catalyst prior to the main manganese dioxide catalyst. If however the manganese dioxide is poisoned, it can be regenerated, returning the catalyst to its previous activity level. The regeneration takes the form of a simple washing procedure which takes advantage of the homogeneous nature of the catalyst and abrades only the top most marked layers, exposing a fresh catalytically active surface.

<u>Pre-Catalyst</u>

In order to prolong the lifetime of the main, manganese dioxide catalyst, it is essential that the contaminants from the gas stream are removed before they come in contact with the catalyst. Larger particles are removed by the fibre glass filter prior to the catalyst but this filter will not remove moisture content, acidic gases or oil mist. A pre-catalyst has therefore been found necessary with a high surface area absorbent in order to refine the incoming gas stream.

Alumina pre-catalyst is found in a wide range of industrial applications as a catalyst support removing hydrocarbons, odorous organic compounds, metal carbonyls and oil mists from gas streams thus making it a suitable candidate for removing contaminants prior to ozone destruct catalyst beds.

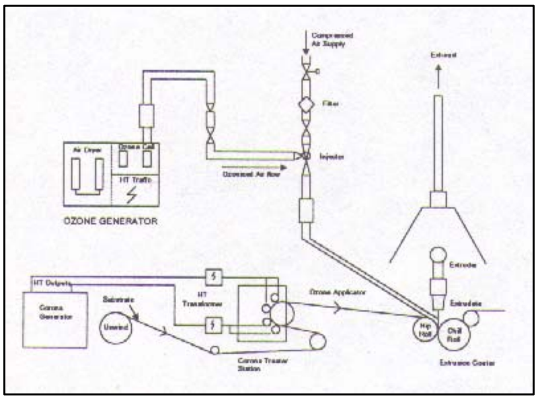
Alumina is a high pore volume inert absorbent the efficiency of which is a function of the gas flow, residence time and gas species to be removed and generally the alumina will remove 0.5 litres of contaminant per Kg of alumina. However, depending upon the application from which the corona treater generated ozone is originating, it is possible to impregnate the alumina to make it more effective as a pre-filter catalyst but experience has shown that dependent upon the application the amount of alumina catalyst required will vary.

Without the alumina pre-catalyst on an ozone elimination unit used with a corona treatment station on a Blown Film extrusion line, the manganese dioxide catalyst will become contaminated with a thin surface layer of polyethylene fines resulting in deactivation of the ozone removing sites. The polyethylene fines pass through the fibre glass filters and coat the top of the catalyst bed. They subsequently react with the ozone in the gas stream leading to oxidative decomposition of the polyethylene and liberate gaseous hydrocarbons which are absorbed downstream of the catalyst bed. The absorbed hydrocarbons block the catalyst surface to the reaction with ozone.

Similar, but not identical, contaminants are present in gas streams from corona treaters in their wide range of industrial applications including coating and printing lines. But, in order to maximise the effectiveness of the pre-catalytic filter, the process application from which the ozone stream originates must be known. Only then can the correct additives be mixed in with the alumina.

OZONE DESTRUCT UNITS AND OZONISERS

Ozone is produced under strictly controlled conditions by ozonisers, to achieve rapid oxidation of a low temperature PE melt, which results in improved bond characteristics between the PE and a paper/board substrate. This is typical in the extrusion coating process for the production of aseptic packaging (Diagram 4).

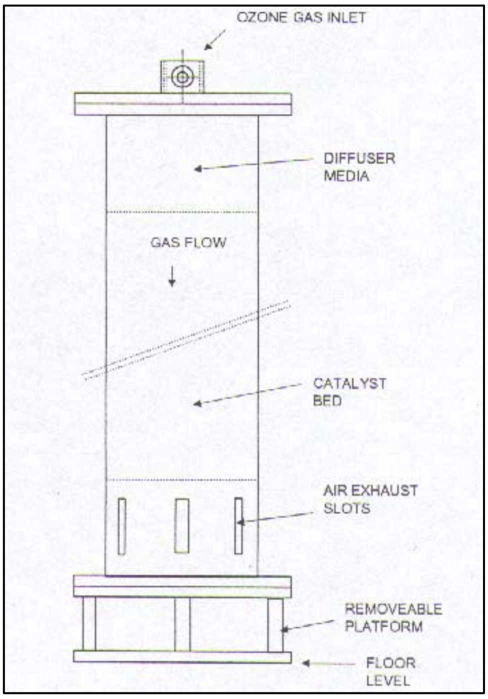


An ozone decomposition device used in conjunction with a corona treater is a high flow - low concentration unit, but when an Ozoniser is stopped from applying ozone to the extrudate for a period of time a low flow - high concentration unit is required (Diagram 5).

The design of the catalyst bed must ensure a much longer dwell time of the gas stream over the catalyst compared to a corona treater application. The typical ratio of the bed length to diameter must be five to one.

The catalyst used, because of the bed length, has to be large. Powder or small granulated catalyst cannot be used due to the very large pressure drops involved. Larger spheres of 6mm diameter with the catalyst coated on them, are the only way to provide an easy path for the gas to pass through whilst providing a long contact time.

So the construction of an ozone destruct unit for an ozoniser is designed with thick walled stainless steel pressure pipe.



CONCLUSION

It is generally accepted that in the long term plant emissions will be prohibited. Waste products, including ozone are increasingly being converted to non-toxic, non-polluting elements inside the plant before discharge to atmosphere.

Ozone destruction units offer the opportunity to prevent an element of atmospheric pollution. They have undergone years of development to ensure their effectiveness with the correct choice of catalyst. Process contaminants in the gas stream can also be successfully filtered with a series of process dependent pre-catalysts to prevent them causing pollution.

With the correct choice of ozone resistant and corrosion proof materials, filters, pre-catalyst and main catalyst, the ozone destruct unit will give years of trouble fre