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(54) A PROCESS OF AND APPARATUS FOR TREATING A LIQUID SUCH AS WATER, WITH OXIDISING GAS

(71) We, W. R. GRACE & CO., a Corporation organised and existing under the Laws of the State of Connecticut, United States of America, of 3 Hanover Square, New York, New York 10004, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a liquid treating system utilizing a pressure-swing system for generating an oxygen enriched gas.

Ozone and oxygen have many uses as purifying and disinfecting agents. They have been used for bleaching, disinfecting and clarifying drinking water, dissipating organics in industrial waste streams prior to disposal and in treatment of municipal waste water to reduce the TOC (total organic carbon) content and COD (chemical oxygen demand). There is no doubt that oxygen and particularly ozone are very effective materials for use in any of these processes. However, no matter how effective they are, they still must compete on a cost basis with other materials and processes. Further description in this application will be directed to waste water treatment, however, it should be borne in mind that the system may be used in combination with essentially any purifying, disinfecting or bleaching operation, municipal or industrial.

A particular problem in waste water treatment is in the TOC (total organic carbon) and COD (chemical oxygen demand) of the treatment plant effluent stream. The COD of this stream should be as low as possible. Ozone and oxygen effectively lower the COD and TOC content of effluents from waste water treatment plants. They remove odours and colour from water and destroy pathogenic organisms. Residual ozone will decompose rather rapidly, since it has a half life of about 20 minutes in water and thereby produces no problems. Tertiary waste treatment using ozone has the potential for

decreasing the waste water treatment time, while considerably decreasing the COD and TOC content, as well as destroying residual bacteria. Secondary waste treatment is more effectively conducted using oxygen than ozone, which is a more severe oxidant and tends to destroy bacteria colonies necessary for effective secondary treatment. Ozone containing gas can at times, however, be used in secondary treatment.

The published prior art in regard to the present process is best evidenced in technical publications of the United States Department of Interior and various literature articles. Repast No. TWRC—4 (PB187758), Ozone Treatment of Secondary Effluents From Wastewater Treatment Plants, is illustrative of an available Department of Interior Report. Illustrative of a literature article is the paper, "Practical Aspects of Water and Waste Water Treatment By Ozone" by E. W. J. Diaper, which was presented at the 162nd National Meeting of the American Chemical Society in Washington, D.C. Other known prior art consists of studies conducted at the Blue Plains Wastewater Treatment Plant in Washington, D.C. These studies have consisted of closed-loop oxygen-ozone treatment of wastewater, using a liquid or compressed oxygen as the initial oxygen source. The present system is a distinct improvement over such prior art systems, and particularly by integrating a pressure-swing system into the closed loop.

The pressure-swing system provides two principal and distinct advantages when introduced into a closed-loop system. Firstly, it provides an efficient method of removing some or all of the nitrogen from air so as to provide an oxygen enriched air stream with an oxygen content of from 30 percent to 95 percent by volume oxygen. The air component which generally is not removed in pressure-swing system is argon, which is present in about a 4 percent to 5 percent content in a 95 percent oxygen stream. This pressure-swing technique provides continuous

[Price 25p]

on site generation of oxygen as needed, using ambient air as the source material. This eliminates the need for large cryogenic storage tanks and having to depend on shipments. The per pound cost of oxygen is also less than when a compressed or cryogenic oxygen source is used.

The second, and probably the most significant, advantage in using a pressure-swing system integrated into the system, is that recycle oxygen enriched air will contain increased nitrogen from having been in contact with the waste water. Waste water will contain dissolved nitrogen due to the partial pressure of nitrogen in the atmosphere, as well as due to formation from waste decomposition. In a closed-loop system, this nitrogen will tend to build up to an equilibrium level which would be about that of the atmosphere exterior to the closed-loop. In order to avoid this nitrogen level build-up in a closed-loop, systems using compressed or cryogenic oxygen as the oxygen source require that all the waste water prior to treatment must undergo an elaborate deaeration technique. This requires a large deaeration chamber, high capacity vacuum pump and a waste water pump not required when a pressure-swing system is used. The pressure-swing system in the present system serves the dual concurrent function of yielding a system which is less complex in equipment and operation, and less costly in regard to initial capital outlay and operation. It produces the required oxygen, while simultaneously maintaining nitrogen at a low level. In this invention, no deaeration step or equipment is required.

According to one aspect of the present invention there is provided a process for treating a liquid, such as water, using an oxidising gas, such a process comprising passing a gaseous stream containing at least oxygen and nitrogen through a pressure-swing system wherein nitrogen is selectively removed therefrom to produce an oxygen enriched gas, passing the oxygen enriched gas to an ozonator to produce an oxygen enriched gas containing from 1 to 7% by weight ozone, passing the oxygen enriched gas containing ozone to at least one contact zone, passing a liquid to be treated to the contact zone, contacting the said liquid with the oxygen enriched gas containing ozone to thereby treat the liquid, removing the treated liquid from the contact zone, and passing excess oxygen enriched gas depleted at least partially of ozone and oxygen from the contact zone.

According to another aspect of the present invention there is provided apparatus for treating a liquid such as water, using an oxidising gas, such apparatus comprising a pressure-swing system for removing nitrogen from a gaseous stream containing at least

oxygen and nitrogen to thereby produce an oxygen enriched gas, an ozonator, a conduit for passing oxygen enriched gas from the pressure-swing system to the ozonator, a first contact zone in which a liquid to be treated can be contacted by an oxygen enriched gas containing ozone, a conduit for supplying oxygen enriched gas containing ozone from the ozonator to the contact zone, a conduit for removing a gas at least partially depleted in ozone and oxygen from the contact zone.

Illustrative embodiments of the invention will now be described with reference to the accompanying drawings, in which:—

Figure 1 is a schematic diagram of a closed-loop ozone treatment system containing one contactor stage;

Figure 2 is a schematic diagram of a system wherein there are two stages of contactors.

In this specification, the effluent from the pressure-swing system will be termed oxygen enriched gas. This term is equivalent to oxygen enriched air.

Referring now to Figure 1 there is shown a system which incorporates a pressure-swing system at a point prior to an ozonator, but subsequent to combining recycle oxygen enriched gas with air. In more detail, fresh air and recycle oxygen rich gas are mixed in pipe 1. This mixture passes through a compressor 2, which increases the pressure of this gas to 25 psig to 150 psig. This gas mixture then passes via a pipe 3 to a chiller 4. Condensed water and the gas mixture pass via a pipe 5 to a separator 6 where the water is removed via a pipe 7. The gaseous mixture, which is now at an increased pressure and fairly dry, passes via a pipe 8 to a pressure-swing system 11. The pressure-swing oxygen system, enclosed in the dash outline in Figure 1, includes at least two absorbent beds designated 9 and 10. The gas mixture is delivered from the pipe 8 to one of the absorbent beds 9 and 10 via the pipe 12 or 13. Two beds are set out here strictly for purposes of simplicity. A three absorbent bed device is very useful, with a four or more absorbent device having certain advantages.

The theory of pressure-swing system is that absorbents have a greater selectivity for at least one component of a mixture. For gaseous fractionation, crystalline aluminosilicate zeolites may be used as the absorbent. These zeolites selectively absorb nitrogen from an air stream, allowing oxygen to pass through the absorbent bed. By the use of two or more absorbent beds, at least one bed can be on an enriched oxygen gas producing phase while one or more beds are being regenerated, that is, depleted of absorbed nitrogen. On completion of the regeneration phase, the absorbent bed is

then switched to the absorbing phase of selectively absorbing nitrogen and producing an oxygen enriched stream. Thereafter, by a selective switching ("swinging") of the absorbent beds from an absorption phase to a regeneration phase and so on, a continuous oxygen enriched stream can be produced. Nitrogen removed from the absorbent bed on regeneration can be passed into the atmosphere. United States Patent Specifications Nos. 3,564,816, 3,237,377, 3,086,339, 3,102,013 3,636,679, 3,104,162, 3,138,439, 3,252,268, 3,142,547 and 2,944,627 illustrate pressure-swing systems which are useful in carrying out the present system.

An oxygen enriched gas exits the pressure-swing system via a pipe 14 or 15 to a main pipe 16. This gas may have a composition of from 30 percent to 95 percent by volume oxygen, with the remainder being argon and other residual components of air. As an example, when this gas is 95 percent oxygen, the residual component will be argon. However, when the enriched gas is from 40 percent to 80 percent oxygen, there will be significant amounts of argon and nitrogen present, as well as minor amounts of other gases. Preferably, the oxygen enriched gas will contain 60 to 90 percent oxygen. The pressure-swing absorbent will also remove any residual amounts of water vapour and carbon dioxide from the input gas.

From pipe 16, the oxygen enriched gas passes into ozonator 17. This may be an ozonator utilizing tubular electrodes or one utilizing flat electrodes. Each operates on the same principal. The oxygen enriched gas is passed between pairs of high potential electrodes and low potential electrodes which are shielded with a dielectric shield. The electrode gap is usually 1 to 3 millimeters. The glow discharge which is maintained in this gap produces the ozone. Depending on the oxygen content of the enriched gas, the ozone content will range from 1 percent to 7 percent by weight. Useful ozone generators are produced by the Welsbach Corporation, Philadelphia, Pa., and the Ozonator Corporation, Batavia, New York. Preferred ozone generators are those of an improved design disclosed in Italian Patent Specification No. 869,360. Such ozone generators have a lower operating cost.

The oxygen enriched gas containing ozone then flows via pipes 18 and 19 to a gas-liquid contactor 20 which constitutes a contact zone. Water to be treated is pumped by a pump 21 through pipes 22 and 23 and into the contact zone 20 where it comes into intimate contact with the oxygen enriched gas containing ozone. The exact contactor construction may vary. This may be a counter-current or cocurrent single or multiple chamber or column continuous type contactor, or it may be a high shear or low

shear batch type contactor. Further, there may be a combination of these techniques. The ozone containing oxygen enriched gas is sparged into the liquid by a means to achieve maximum exchange of the oxygen and ozone into the water. These are not critical and actually any effective type of gas-liquid contacting system can be used. In most instances, other plane requirements will dictate the type of contact used.

Purified water exits the contactor chamber via a pipe 24. A recycle gas composed of a partially oxygen enriched gas which now contains an increased nitrogen level due to the partial depletion of oxygen and transfer of dissolved nitrogen from the treated water, exits the contact chamber via a pipe 25. This gas may optionally pass through a heater 26 to decompose any residual ozone. Thereafter, the recycle gas flows by a pipe 27 to pipe 1 for mixture with air in pipe 1 and a repeat of the cycle.

Figure 2 shows a modified form of the system shown in Figure 1. In Figure 2, there is shown an additional contactor, with contactor 30 being waste water secondary treatment contactor and contactor 20 being tertiary treatment contactor. The input waste material will be effluent from a primary waste treatment stage and is pumped by a pump 21 via a conduit 22 to contactor 30. This contactor is of a type similar to contactor 20. After thorough contacting, effluent water from contactor 30 flows via pipe 31 to a separator 32 where any solid sludge material in the effluent stream is separated out and returned via a conduit 34 to contactor 30. Separator 32 is particularly necessary when activated sludge processing is carried out in contactor 30. Effluent water flows from separator 32 via conduits 33 and 23 to contactor 20 for tertiary treatment which is essentially a disinfection of the water. Ozone containing oxygen enriched gas flows via conduits 18 and 19 and valve 29 to contactor 20. The contacting of the bacteria laden input water with ozone oxidatively destroys this bacteria and also oxidatively destroys remaining organics, some of which are responsible for a slight colouration of the input water to contactor 20. Treated water exits at 24, with at least a partially ozone depleted oxygen rich gas exiting at 25 for passage through heater 26 which decomposes any residual ozone. This gas is then conducted by valve 35 and conduit 36 to contactor 30. Additional oxygen is supplied to the gas via conduit 16 and valve 35, which oxygen enriched gas flows directly from the pressure-swing system 11. Some additional oxygen will usually have to be added to the gas stream input to contactor 30. This oxygen enriched gas is thoroughly contacted with the waste liquid mixture in contactor 30 so that the off-gas is substanti-

ally depleted in oxygen. Depending on the oxygen content of the off-gas from the contactor 30, this gas is either vented at 34 or recycled by conduits 38 and 27 and valve 37 to air input at 1.

This process is essentially a countercurrent flow of the waste water material to be treated and the treating oxidizing gas. A strong oxidant such as ozone is necessary for effective tertiary treatment. However, in secondary waste treatment, which usually consists of an activated sludge technique, a strong oxidant such as ozone would destroy the bacteria which are necessary for effective secondary waste treatment processes. Ozone is used mainly for final disinfection treatment (tertiary). However, if solely an oxidative reaction (non-bacterial) process is being conducted in contactor 30, ozone containing oxygen enriched gas could also be used in this process operation. In such an instance, ozone decomposition heater 26 would be deleted and ozone containing gas flowed from contactor 20, and/or ozone containing oxygen enriched gas flowed directly from the ozonator.

In another embodiment using the system of Figure 2, concurrently with ozone containing oxygen enriched gas flow to contactor 20, an oxygen enriched gas is passed from the pressure-swing system via conduits 16 and 36 and valve 35 to contactor 30. After thorough contacting, the off-gas from contactor 30 flows by conduits 38 and 27 and valve 37 to air input at 1. The off-gas from contactor 20 in this embodiment will flow through conduit 25 to heater 26 to destroy any residual ozone, and then by conduits 39 and 27 via valve 37 to air input at 1. In this embodiment, there is no flow of oxygen enriched gas from contactor 20 to contactor 30.

If necessary in the system of Figure 2 an oxygen enriched gas can be flowed to contactor 20 without passage through the ozonator. This oxygen enriched gas is flowed to contactor 20 through conduits 28 and 19 via valve 29. This feature of the process allows for an oxygen enrichment of the ozone containing gas which is beneficial when the off-gas from contactor 20 is to be flowed to contactor 30, and when the ozonator is out of use for any reason. Further it may be desirable to provide a valve between the pipe 16 and the ozonator, to prevent air from the pressure swing system flowing to the ozonator.

The amount of flows of waste water and oxygen enriched gas to contactor 30 and impure water and ozone containing oxygen enriched gas to contactor 20 will depend on the degree of contaminant content of these waste streams, the content of ozone and/or oxygen in the gas streams, and the effectiveness of the oxygen and ozone contacting

apparatus. Generally, municipal waste treatment plants require 0.25 to 1 ton oxygen for each million gallons of waste water to be treated. This would be for oxygen secondary waste water treatment and oxygen-ozone tertiary treatment. The amount of oxygen enriched gas does not have to be closely controlled in this process, since excess oxygen enriched gas is recycled for reuse. Most systems which use oxygen vent the off-gas to the atmosphere, thereby losing a valuable process material. For this reason, it is preferred to operate at a 10 to 50 percent excess of oxygen relative to the total biological and chemical oxygen demands. The use of excess oxygen will also increase the oxygen content of the treated water flowing from the system which is ecologically beneficial. When industrial wastes are being treated, the desirable quantity of oxygen relative to the waste material to be treated can easily be calculated after analysis of the waste stream.

The system of Figure 1 or Figure 2 can be operated continuously, since the pressure-swing system continuously determines the nitrogen gas level in the system. This nitrogen level in the closed-loop system can be maintained constant, regardless of the dissolved nitrogen content of the water which undergoes treatment or the degree of nitrogen evolution during treatment. In essence, this nitrogen level adjustment is an automatic and inherent feature of this system. Depending on the adjustment of the pressure-swing oxygen system, the amount of nitrogen removed can range from 10 percent to essentially complete removal.

In more detail concerning the pressure-swing system, preferred devices are set out in United States Patent Specifications Nos. 3,086,339 and 3,142,547. These Patent Specifications set out improvements on the device of United States Patent Specification No. 2,944,627. The basic pressure-swing systems consist of essentially two phases, the absorption phase and the regeneration phase. The absorption phase can be optimized by maintaining the bed temperature at about ambient or below, and allowing the column to approach the breakthrough point prior to swinging. The breakthrough point is that point where the absorbent is at full capacity. These are the principal operational techniques for optimizing the absorption phase. However, there are many techniques that can be utilized to optimize the regeneration phase. Regeneration is the removal of the absorbed component from the absorbent bed. Steps which are conducted during regeneration are a depressurization of the absorbent bed to ambient pressure or below and the flowing of a purge gas through the absorbent bed. Optionally, the bed may also be heated. United States Patent Specification No. 130

2,944,627 discloses the feature of using a portion of product gas from a bed. This product gas may flow directly from the absorbent bed on the absorbing phase or from a purge tank. In United States Patent Specification No. 3,142,547 there is disclosed a method of using depressurizing gas as an effective backwash or purge gas. Depressurizing gas will have a higher oxygen content than input gas and, as such, will be a good purge medium. By the use of the depressurizing gas along with product gas as the purge gas, the pressure-swing system is made more economical. United States Patent Specification No. 3,086,339 discloses a three absorbent bed system utilizing a depressurization gas and a product gas purge. Such a system will produce oxygen enriched gas in a fairly high volume. In a further development a two absorbent bed-single tank system which utilizes a dual sequential bed pressure equalization technique and is very efficient in conserving product gas.

The absorbent used in the absorbent beds of these pressure-swing systems is usually a synthetic zeolite such as Zeolite A, X or Y exchanged with potassium, alkali earth ions, rare earth ions, transition metal ions or mixtures of these ions; or a naturally occurring zeolite such as erionite, mordenite, chabazite, gmelinite, heulandite or faujasite in its natural or metal ion exchanged form. Very useful absorbents are alkaline earth exchanged Zeolite A and Zeolite X, and particularly these zeolites exchanged with calcium, barium and strontium ions.

In one embodiment input air and recycle gas are mixed and compressed to a pressure of 25 psig to 50 psig. This compressed gas is passed through the condenser where water vapor is removed as liquid water, and thereafter to the pressure-swing fractionator. The ratio of air to recycle gas in this mixture will depend on the amount of oxygen needed to replace that which has been converted to ozone and that used in the contacting step. In general, air will have to be added in a ratio of 5 to 10 times the amount of oxygen that is required to replace that used in the previous cycle. Since air is only about 20 percent oxygen at least 5 volumes of air must be added for each volume of oxygen required. Higher volumes of air are usually added, since some of the oxygen enriched product gas from the pressure-swing fractionator is normally used as a purge gas within the fractionator. The dried air-recycle gas mixture then passes through the pressure-swing system where nitrogen is decreased in concentration or fully removed. At this stage, essentially all carbon dioxide and water vapour are removed. The resulting oxygen enriched gas, now containing 60 to 90 percent by volume oxygen, is fed to the ozonator. The ozonator effluent con-

tains 3 to 6 percent by weight azone, with the oxygen content being decreased 4.5 to 9 percent by volume. This gas flows to the contractor, where it is thoroughly contacted with water. Continuous cocurrent contacting of the water and oxygen enriched gas containing ozone provides maximum contact and use of ozone. During this contacting, dissolved nitrogen leaves the water phase, with ozone and some oxygen being dissipated in the water phase. The resulting nitrogen enriched gas froms the recycle gas, which is combined with air for initiation of another cycle.

The recycle gas loop can optionally contain gas scrubber or drier means. That is, this part of the system can contain gas scrubbers for carbon dioxide and carbon monoxide, and a chiller or absorptive drier to remove some of the water content. A suitable absorptive drier material is silica gel.

As is evident, this system could be used for any liquid treatment. However, it is most effective in water purification treatment. This can consist of producing potable water, or the treatment of industrial or municipal waste streams. In the treatment of municipal waste streams, this system can be used for secondary or tertiary treatment or both.

WHAT WE CLAIM IS:—

1. A process for treating a liquid, such as water, using an oxidising gas, such a process comprising passing a gaseous stream containing at least oxygen and nitrogen through a pressure-swing system wherein nitrogen is selectively removed therefrom to produce an oxygen enriched gas, passing the oxygen enriched gas to an ozonator to produce an oxygen enriched gas containing from 1 to 7% by weight ozone, passing the oxygen enriched gas containing ozone to a contact zone, passing a liquid to be treated to the contact zone, contacting the said liquid with the oxygen enriched gas containing ozone to thereby treat the liquid, removing the treated liquid from the contact zone, and passing excess oxygen enriched gas depleted at least partially of ozone and oxygen from the contact zone.

2. A process as claimed in claim 1 in which the excess oxygen enriched gas from the contact zone is fed as a recycle gas and mixed with air, the resultant mixture being passed to the pressure-swing system and thereafter repeating the cycle.

3. A process as claimed in claim 1 in which the excess oxygen enriched gas from the contact zone is fed to an additional contact zone to contact a further liquid to be treated, and thereafter venting the gas which is further depleted in oxygen or mixing the gas with air and passing the resultant mixture to the pressure-swing system and thereafter repeating the cycle.



2,944,627 discloses the feature of using a portion of product gas from a bed. This product gas may flow directly from the absorbent bed on the absorbing phase or from a purge tank. In United States Patent Specification No. 3,142,547 there is disclosed a method of using depressurizing gas as an effective backwash or purge gas. Depressurizing gas will have a higher oxygen content than input gas and, as such, will be a good purge medium. By the use of the depressurizing gas along with product gas as the purge gas, the pressure-swing system is made more economical. United States Patent Specification No. 3,086,339 discloses a three absorbent bed system utilizing a depressurization gas and a product gas purge. Such a system will produce oxygen enriched gas in a fairly high volume. In a further development a two absorbent bed-single tank system which utilizes a dual sequential bed pressure equalization technique and is very efficient in conserving product gas.

The absorbent used in the absorbent beds of these pressure-swing systems is usually a synthetic zeolite such as Zeolite A, X or Y exchanged with potassium, alkali earth ions, rare earth ions, transition metal ions or mixtures of these ions; or a naturally occurring zeolite such as erionite, mordenite, chabazite, gmelinite, heulandite or faujasite in its natural or metal ion exchanged form. Very useful absorbents are alkaline earth exchanged Zeolite A and Zeolite X, and particularly these zeolites exchanged with calcium, barium and strontium ions.

In one embodiment input air and recycle gas are mixed and compressed to a pressure of 25 psig to 50 psig. This compressed gas is passed through the condenser where water vapor is removed as liquid water, and thereafter to the pressure-swing fractionator. The ratio of air to recycle gas in this mixture will depend on the amount of oxygen needed to replace that which has been converted to ozone and that used in the contacting step. In general, air will have to be added in a ratio of 5 to 10 times the amount of oxygen that is required to replace that used in the previous cycle. Since air is only about 20 percent oxygen at least 5 volumes of air must be added for each volume of oxygen required. Higher volumes of air are usually added, since some of the oxygen enriched product gas from the pressure-swing fractionator is normally used as a purge gas within the fractionator. The dried air-recycle gas mixture then passes through the pressure-swing system where nitrogen is decreased in concentration or fully removed. At this stage, essentially all carbon dioxide and water vapour are removed. The resulting oxygen enriched gas, now containing 60 to 90 percent by volume oxygen, is fed to the ozonator. The ozonator effluent con-

tains 3 to 6 percent by weight azone, with the oxygen content being decreased 4.5 to 9 percent by volume. This gas flows to the contractor, where it is thoroughly contacted with water. Continuous cocurrent contacting of the water and oxygen enriched gas containing ozone provides maximum contact and use of ozone. During this contacting, dissolved nitrogen leaves the water phase, with ozone and some oxygen being dissipated in the water phase. The resulting nitrogen enriched gas froms the recycle gas, which is combined with air for initiation of another cycle.

The recycle gas loop can optionally contain gas scrubber or drier means. That is, this part of the system can contain gas scrubbers for carbon dioxide and carbon monoxide, and a chiller or absorptive drier to remove some of the water content. A suitable absorptive drier material is silica gel.

As is evident, this system could be used for any liquid treatment. However, it is most effective in water purification treatment. This can consist of producing potable water, or the treatment of industrial or municipal waste streams. In the treatment of municipal waste streams, this system can be used for secondary or tertiary treatment or both.

WHAT WE CLAIM IS:—

1. A process for treating a liquid, such as water, using an oxidising gas, such as a process comprising passing a gaseous stream containing at least oxygen and nitrogen through a pressure-swing system wherein nitrogen is selectively removed therefrom to produce an oxygen enriched gas, passing the oxygen enriched gas to an ozonator to produce an oxygen enriched gas containing from 1 to 7% by weight ozone, passing the oxygen enriched gas containing ozone to a contact zone, passing a liquid to be treated to the contact zone, contacting the said liquid with the oxygen enriched gas containing ozone to thereby treat the liquid, removing the treated liquid from the contact zone, and passing excess oxygen enriched gas depleted at least partially of ozone and oxygen from the contact zone.

2. A process as claimed in claim 1 in which the excess oxygen enriched gas from the contact zone is fed as a recycle gas and mixed with air, the resultant mixture being passed to the pressure-swing system and thereafter repeating the cycle.

3. A process as claimed in claim 1 in which the excess oxygen enriched gas from the contact zone is fed to an additional contact zone to contact a further liquid to be treated, and thereafter venting the gas which is further depleted in oxygen or mixing the gas with air and passing the resultant mixture to the pressure-swing system and thereafter repeating the cycle.



4. A process as claimed in claim 3, in which the liquid treated in the additional contact zone is passed to the first mentioned contact zone for further treatment in the first mentioned contact zone.

5. A process as claimed in claim 3 or 4, in which oxygen enriched gas is mixed with the gas leaving the first mentioned contact zone, and passing the resulting mixture to the additional contact zone.

6. A process as claimed in claim 1 or 2, in which only a portion of the oxygen enriched gas from the pressure-swing system is passed to the ozonator, the remaining portion thereof being passed to a further contact zone to treat further liquid therein, excess oxygen enriched gas from the further contact zone being fed as a recycle gas and mixed with air, the resultant mixture being passed to the pressure-swing system and the cycle being thereafter repeated.

7. A process as claimed in claim 6, in which the pressure of the gaseous mixture containing recycle gas and air is increased to a pressure of between 25 psig and 150 psig.

8. A process as claimed in any one of the preceding claims, in which the liquid to be treated is water and dissolved nitrogen in the water mixes with the oxygen enriched gas containing ozone in the first mentioned contact zone to thereby increase the nitrogen content of the gas.

9. A process as claimed in any one of the preceding claims, in which residual amounts of carbon dioxide and water vapour are removed during the passage of the gas through the pressure-swing system.

10. A process as claimed in any one of the preceding claims, in which the oxygen enriched gas from the pressure-swing system contains from 30 to 95% by volume oxygen.

11. A process as claimed in claim 7 in which water in the gaseous mixture having the increased pressure is removed by condensation.

12. Apparatus for treating a liquid such as water, using an oxidising gas, such apparatus comprising a pressure-swing system for removing nitrogen from a gaseous stream containing at least oxygen and nitrogen to thereby produce an oxygen enriched gas, an ozonator, a conduit for passing oxygen enriched gas from the pressure-swing system to the ozonator, a first contact zone in which a liquid to be treated can be contacted by an oxygen enriched gas containing ozone, a conduit for supplying oxygen enriched gas

containing ozone from the ozonator to the contact zone, a conduit for removing a gas at least partially depleted in ozone and oxygen from the contact zone.

13. Apparatus as claimed in claim 12, which includes means in which the gas from the contact zone is mixed with air, and a conduit for passing such a mixture to the pressure-swing system thereby producing a closed-loop system for the treatment of a liquid.

14. Apparatus as claimed in claim 12, which includes a further gas-liquid contact zone, a conduit for passing gas from the first contact zone to the further contact zone, a conduit for passing gas further depleted in oxygen from the further contact zone as a recycle gas, and a conduit for passing a liquid treated in the further contact zone to the first contact zone for further treatment.

15. Apparatus as claimed in claim 14, which includes a compressor for passing a mixture of air and recycle gas from a mixing means to the pressure-swing system, the compressor also acting to increase the pressure of the said mixture.

16. Apparatus as claimed in claim 14 or 15, which includes a conduit for passing oxygen enriched gas from the pressure-swing system to the further contact zone.

17. Apparatus as claimed in any one of claims 12 to 16, in which the pressure-swing system contains at least three absorbent beds, each bed containing a zeolite absorber.

18. Apparatus as claimed in claim 17, in which the pressure-swing system contains at least three absorbent beds, each bed containing a zeolite absorber.

19. Apparatus as claimed in claim 18 which includes a water vapour removing device positioned between the compressor and the pressure-swing system.

20. Apparatus as claimed in claim 19 in which the water vapour removing device is a compressor.

21. A process for treating a liquid substantially as described herein with reference to the accompanying drawings.

22. Apparatus for treating a liquid, such apparatus being constructed and arranged substantially as described herein with reference to and as shown by the accompanying drawings.

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