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(54) **Title:** REDUCTION OF NO_x EMISSIONS BY EFFLUENT GASES FROM FERTILIZER PRODUCTION WITH OZONE INJECTION AND WET SCRUBBING

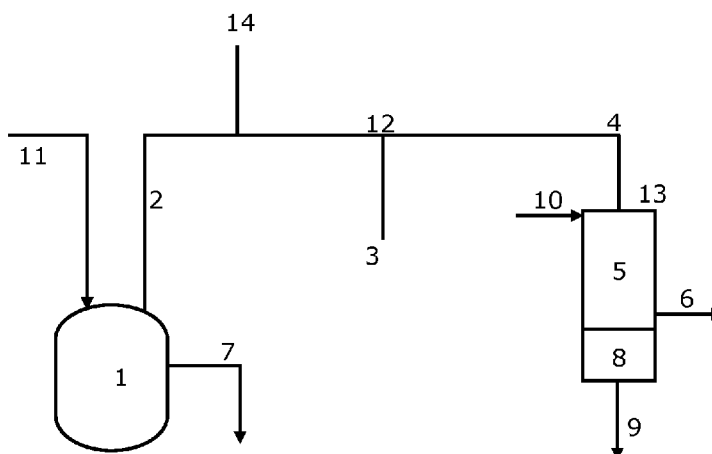


FIG. 2

(57) **Abstract:** The invention concerns a process for the removal of NO_x from gaseous effluents generated in the production of fertilizer. The composition of the NO_x in this gaseous effluent is rich in NO₂. The process comprises the steps of treating the gaseous effluent with ozone and oxidizing NO and NO₂ present in the NO_x to higher nitrogen oxides, and, passing the resultant gas mixture through a wet scrubber and removing the higher nitrogen oxides. The invention further concerns the use of ozone as an oxidant in the removal of NO_x from a gaseous effluent generated in fertilizer production; and a fertilizer production plant, designed to remove NO_x from the gaseous effluent that is generated in the running of that plant.

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REDUCTION OF NOX EMISSIONS BY EFFLUENT GASES FROM
FERTILIZER PRODUCTION WITH OZONE INJECTION AND WET SCRUBBING

5 The invention relates to the technical field of NO_x removal from gaseous effluents.
The invention more specifically relates to the removal of NO_x from gaseous effluents
generated in the production of fertilizer. This gaseous effluent has a specific
composition with NO_x, rich in NO₂. The invention is advantageous for pollution
control in fertilizer production.

10 **BACKGROUND**

During the production of fertilizers, NO_x gasses are formed as an unwanted side
product. NO_x can lead to acid rain formation. Addition of urea, a well-known method
of reducing NO_x emissions, decreases NO_x production during the production of
15 fertilizer but increases N₂O emission. N₂O is a greenhouse gas, affecting global
warming much more than CO₂. The effect of these gasses on global warming is
expressed by a global-warming potential or GWP value for each gas, indicating how
many times the impact of 1 ton of CO₂ needs to be multiplied by to have the same
impact as 1 ton of that gas and this for a period of 100 years after the gas has been
20 released in the atmosphere. For N₂O, the GWP_(100 years) is equal to 298. Therefore,
other methods for reducing NOX are needed that do not increase the emission of
other environmentally harmful gasses or chemicals.

As NO₂ is the main component of the NO_x that is released by fertilizer production,
25 typically for the nitrophosphate process, especially the NO₂ needs to be eliminated
from the gaseous effluent produced by fertilizer production before the gaseous
effluent can be released in the atmosphere. Gaseous effluents from fertilizer plants
are relatively cold and typically also comprise dust particles, acid droplets,
hydrofluoric acid and water; all of which can cause complications.

30 From the prior art, methods are known to chemically react NO_x from fertilizer plant
off gasses, based on selective catalytic reduction (SCR). The drawback of these
methods is that expensive catalysts need to be used and catalyst regeneration cycles
need to be carried out. Hence, there still is a desire for alternatives.

35 Methods to treat NO_x containing gaseous effluents of other industrial processes have
been described in the prior art, with the difference that the NO_x composition is rich
in NO and low in NO₂. Not many other components are present in the gaseous

effluents that interfere with the oxidation reaction. Typically, NO_x is removed from gaseous effluents by alkaline scrubbing. The gaseous effluent produced by fertilizer production comprises a large amount of acidic components, preferably nitric acid, hydrochloric acid, hydrofluoric acid, silicon tetrafluoride and carbon dioxide (CO_2).
5 These acidic components will react with the alkaline medium in the scrubber, and as a consequence large amounts of alkaline medium are needed, producing large amounts of side products. Therefore, this technique is unsuitable to be used to reduce NO_x pollution during fertilizer production.

10 US 6,231,824 for instance, describes a 3-step process for the reduction of NO_x in a furnace flue gas. First, the gaseous effluent is passed through a solid catalyst where NO is converted to NO_2 . This is followed by the oxidation of NO_2 by ozone to N_2O_5 before a wet scrubber removes the N_2O_5 from the gaseous effluent. The oxidation reaction is carried out with a large excess of ozone, namely in excess of 1.5
15 equivalents as theoretical 0.5 equivalents should be sufficient. This process is unsuitable for the treatment of low temperature gaseous effluents from a fertilizer plant that comprise dust particles that can clog up the solid catalyst and droplets of acid that can poison the catalyst.

20 US 5,985,223 describes the removal of SO_x and NO_x from a gaseous effluent generated by a metal pickling process. The composition of the NO_x is 60 to 65 vol% NO and 35-40 vol% NO_2 . The gaseous effluent is passed through a first alkaline scrubber to remove at least part of the NO_2 before oxidation is carried out by ozone. Finally the gaseous effluent is passed through a second alkaline scrubber to remove
25 N_2O_5 . Passing through the first scrubber makes the NO_x composition richer in NO . The composition obtained is not provided. The use of two alkaline scrubbers makes the removal of NO_x from a gaseous effluent complex and expensive. Furthermore, the whole installation takes up a large volume, making it difficult to amend existing plants.

30 EP1040863 and EP0532207 describe the removal of SO_x and NO_x from exhaust gas from fossil fuel fired boiler containing 95 % NO and 5 % NO_2 . The disclosed method involves oxidation with ozone in stoichiometric excess at an elevated temperature and thereafter treatment with liquid.

35 It is therefore an object of the invention to overcome at least some of the problems mentioned above for the removal of NO_x from fertilizer production gaseous effluents.

The invention aims to develop a method and installation that can be used specifically for the removal of NO_x from gaseous effluents generated in fertilizer production.

SUMMARY OF THE INVENTION

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In a first aspect, the invention provides in a process for the removal of NO_x from a gaseous effluent generated in the production of fertilizer, comprising the steps of:

- a) contacting the gaseous effluent with 0.7 to 1.4 equivalents ozone to every 1 equivalent of NO_x present in said gaseous effluent for 0.5 to 15
10 seconds, providing in a resultant gas mixture, wherein NO and NO₂ present in the NO_x are oxidized to higher nitrogen oxides; and
- b) passing the resultant gas mixture through a wet scrubber thereby removing the higher nitrogen oxides,

15 wherein the gaseous effluent generated in the production of fertilizer has a NO_x composition of 80 to 100 mole% NO₂ and 0 to 20 mole% NO.

A method according to the invention is advantageous as with ozone treatment of the off gasses of the fertilizer production, a way is provided to reduce NO_x emissions without increasing N₂O emissions. This "pre-ozonation" method is thus a method to
20 intensify NO_x removal. Furthermore, applying ozone to remove NO_x from off-gases originating from the phosphate rock digestion process is an effective and safe solution.

The term "fertilizer" refers to a material from an at least partially synthetic origin that is intended to be applied to soil or plants to supply one or more plant nutrients.
25 The fertilizer can be of the single nutrient type, for example a nitrate salt, or from the multi-nutrient type. Examples of multi-nutrient type fertilizers are: NP fertilizers preferably monoammonium phosphate or diammonium phosphate, NK fertilizers preferably potassium nitrate, PK fertilizers preferably a monopotassium phosphate or
30 dipotassium phosphate, or NPK fertilizer, comprising nitrogen, phosphorus and potassium compounds.

The term "gaseous effluent" refers to gas molecules, dust particles, droplets that are released from and during a chemical or physical process.

35

The term "NO_x" refers to the sum of all the mono-nitrogen oxides present in the gaseous effluent.

The following chemical formulas are used:

- NO, meaning nitrogen oxide;
- NO₂, meaning nitrogen dioxide;
- 5 - NO₃, meaning nitrogen trioxide;
- N₂O₃, meaning dinitrogen trioxide;
- N₂O₄, meaning dinitrogen tetroxide;
- N₂O₅, meaning dinitrogen pentoxide.

10 The term "higher nitrogen oxides" refers to nitrogen oxides as product from an oxidation reaction wherein the nitrogen atom has a higher oxidation state than the nitrogen atom in the reagent. The term is always relative to the reagent that is oxidised. For example, N₂O₅, where the nitrogen atom has an oxidation state of +5, is a higher nitrogen oxide of NO₂, where the nitrogen atom has an oxidation state of
15 +4, and NO₂ is a higher nitrogen oxide of NO, where the nitrogen atom has an oxidation state of +2.

The term "contacting" means adding one gas mixture to another and letting the two gas mixture mix with each other. This can be achieved by injecting one gas mixture
20 in the other. The mixing can be passively, by the turbulence caused by the addition of the gas, or actively, where a mechanical movement causes the gasses to mix with each other.

The gaseous effluent generated in the production of fertilizer has a composition that
25 is different from other chemical processes releasing NO_x. The gaseous effluent generated in fertilizer production comprises NO_x, and these NO_x have a composition rich in NO₂, preferably 80 to 100 mole% NO₂ and 0 to 20 mole% NO, more preferably 90 to 95 mole % NO₂ and 5 to 10 mole % NO. In addition to NO_x, the gaseous effluent also comprises water vapour, hydrogen fluoride (HF), silicon
30 tetrafluoride (SiF₄), carbon dioxide, droplets of nitric acid (HNO₃) and/or dust. The specific composition of the gaseous effluent and the variation of this composition during the production of fertilizer requests specific reaction conditions. As the NO_x in the gaseous effluent is rich in NO₂, less ozone needs to be used compared to other gaseous effluents with NO_x compositions that are rich in NO known from the prior
35 art. The exact amount of ozone that needs to be used can't be deduced based on the NO_x composition alone, other elements preferably other components in the gaseous effluent and external factors preferably humidity and external temperature need to be taken into account.

The ozone is contacted to the gaseous effluent in a molar ratio of ozone over NO_x in the gaseous effluent of 0.7 to 1.4, preferably 0.8 to 1.4, more preferably 0.9 to 1.3, most preferably 0.9 to 1.2 and typically 1.0.

5

Molar ratios in this region are an equilibrium between enough ozone to drive the oxidation of NO_x forward in the presence of all the other components in the gaseous effluent and minimizing the amount of ozone that needs to be generated and is not used in the oxidation reaction itself. The excess of ozone after the oxidation needs to be removed from the gaseous effluent requesting energy and resources. This and the fact that the ozone needs to be generated at first makes the use of a large excess of ozone cost-inefficient.

In a preferred embodiment of a process according to the invention, the fertilizer production is the acid digestion of phosphate ore. Preferably the fertilizer is produced by nitric acid treatment of apatite. In another preferred embodiment, the dissolution or digestion of phosphorous containing rocks is carried out by treatment with nitric acid or nitric acid in combination with other acids, typically, but not exclusively phosphoric acid or sulphuric acid. This process is called the mixed acid digestion process.

In a possible embodiment of a process according to the invention, the higher nitrogen oxide is N_2O_5 .

This is advantageous since N_2O_5 can be easily removed from the gaseous effluent by a wet scrubber.

In an advantageous process embodiment according to the invention, the medium used in the wet scrubber is reclaimed water, meaning water that have been used before. More preferably the water has been used to clean at least parts of the fertilizer production plant, preferably reactors, pipes or the floors of the plant. Salts and other components related to fertilizer production will be dissolved in said water. Most preferably, the reclaimed water is acidic.

In an advantageous process embodiment according to the invention, the wet scrubber is an acidic wet scrubber.

A first advantage of using an acidic solution in the scrubber is that not all the acidic components that are present in the gaseous effluent generated in fertilizer production will react and/or be absorbed by the medium. The gaseous effluent comprises large amounts of carbon dioxide, hydrochloric acid, hydrofluoric acid or silicon tetrafluoride. The acidic medium will still absorb the higher nitrous oxides, but less side products will be formed in the acidic medium. Eventually this results in less medium that needs to be used in the scrubber and less side products that needs to be disposed of.

10 In a possible embodiment according to the invention, the gaseous effluent comprises at least one of the following list: water vapour, hydrogen fluoride, silicon tetrafluoride, nitric acid or dust.

The advantage thereof is that the gaseous effluent can be directly treated in the method without any purification steps in advance. Another advantage is that the method can be carried out in almost every existing wet scrubber modified in that an ozone injection point is fitted in the gaseous effluent supply line to the scrubber. If a pre-treatment was needed, large structures will need to be positioned between the source of the gaseous effluent and the scrubber. This makes it difficult to modify existing installations.

In a preferred process embodiment according to the invention, the scrubber in step b) is the only scrubber used for the removal of NO_x from the gaseous effluent.

25 This has the advantage that only one scrubber needs to be installed. It reduces the running costs of the removal of NO_x as only one scrubber needs to be maintained and provided with water or scrubbing solution. This also reduces the amount of water or scrubbing solution that needs to be treated or purified after it has fulfilled its role in the scrubber. The solution provided is cost effective and environmentally friendly.

In an even more preferred embodiment, the scrubber solution, which is a concentrated acidic liquid containing nitrates, is recycled into the fertilizer production process. By doing so, there is no waste stream.

35 In an embodiment of a process according to the invention, nitric acid, nitrous acid or a salt thereof is formed in step b).

The formation of nitric acid, nitrous acid or a salt hereof has the advantage that these species have a high solubility in water and therefore can be removed effectively from the gaseous effluent by a wet scrubber. The water comprising the components can be used as an acid solution or the salts can be used as fertilizer.

5

In the process according to the invention, the time between the gaseous effluent being mixed with the ozone of step a) and entry of the resultant gas mixture in the wet scrubber of step b) is 0.5 to 15 seconds, preferably 3 to 15 seconds, more preferably 4 to 13 seconds, most preferably 5 to 11 seconds, typically 7 seconds.

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In a preferred embodiment of a process according to the invention, the temperature in step a) is 130 °C or less, preferably less than 100 °C, more preferably less than 50 °C.

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In a preferred embodiment the time is 4 to 13 seconds at a temperature of less than 100 °C.

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A temperature below 130 °C reduces the destruction of ozone. Therefore more ozone is available for oxidation of NO_x. At lower temperatures less ozone needs to be generated to obtain the same efficacy of the removal of NO_x from the gaseous effluent. A higher temperature also pushes the reaction equilibrium towards the reagents side, promoting the decomposition of N₂O₅ back towards NO₂.

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In an advantageous embodiment of a process according to the invention, a gas analyser measures the concentration of NO_x in the gaseous effluent and regulates the amount of ozone added to the gaseous effluent in step a) on the basis of the NO_x concentration measured.

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Measuring the concentration of NO_x in the gaseous effluent determines the amount of NO_x present in the gaseous effluent at a certain point in time. This information is used to determine how much ozone needs to be added to the gaseous effluent at that point in time. This has the advantage that at any point in time the correct amount of ozone is added to the gaseous effluent so that a certain ratio of moles of ozone to the moles of NO_x is maintained. This prevents the over or under dosing of ozone, preventing ozone spillage or incomplete oxidation of the NO_x.

35

In a second aspect, the invention provides the use of ozone as an oxidant for the oxidation of NO_x in a gaseous effluent, wherein the gaseous effluent is generated in

fertilizer production, wherein the gaseous effluent generated in the production of fertilizer has a NO_x composition of 80 to 100 mole% NO_2 and 0 to 20 mole% NO .

5 The use of ozone has the advantage that it can be generated on the spot and no chemicals need to be stored, supplied or disposed of.

10 In a preferred use according to the invention, NO_x is removed from a gaseous effluent generated in the fertilizer production by means of oxidation by ozone of NO and NO_2 present in the NO_x to higher nitrogen oxides, providing in a resultant gas mixture, and scrubbing the resultant gas mixture by means of a wet scrubber thereby removing the higher nitrogen oxides

15 NO_x gets oxidised by ozone to higher nitrogen oxides. These higher nitrogen oxides are more water soluble and can be removed easily by a wet scrubber.

20 In an advantageous use according to the invention, the fertilizer production is the acid digestion of phosphate ore; preferably nitric acid treatment of apatite. In another preferred embodiment, the fertilizer production is the dissolution or digestion of phosphorous containing rocks, carried out by treatment with nitric acid or nitric acid in combination with other acids, typically, but not exclusively phosphoric acid or sulphuric acid. Most preferred, the fertilizer production is the digestion of phosphate ore with nitric acid as the only acid used.

25 The digestion of phosphate ore is one of the main processes to obtain phosphate for fertilizer production, especially in the production of NP and NPK fertilizers. The main source of phosphate ore is apatite, and preferably this apatite is treated with nitric acid. The use of nitric acid in the digestion of phosphate ore is favoured over the use of sulphuric acid as no phosphogypsum is formed. The phosphogypsum has no economic value, and due to its weakly radioactive nature precautions need to be taken for the disposal of it.

30 The ozone is used in a molar ratio of ozone over NO_x in the gaseous effluent of 0.7 to 1.4, preferably 0.8 to 1.4, more preferably 0.9 to 1.3, most preferably 0.9 to 1.2 and typically 1.0.

35 Molar ratios in this region are an equilibrium between enough ozone to drive the oxidation of NO_x forward in the presence of all the other components in the gaseous effluent and minimizing the amount of ozone that needs to be generated and is not

used in the oxidation reaction itself. The excess of ozone after the oxidation needs to be removed from the gaseous effluent requesting energy and resources. This and the fact that the ozone needs to be generated at first makes the use of a large excess of ozone cost-inefficient.

5

In a use according to the invention, the gaseous effluent comprising the oxidation products of NO_x is fed to a wet scrubber. The oxidation products of NO_x are higher nitrogen oxides, preferably N_2O_5 . These higher nitrogen oxides are much more water soluble than NO and NO_2 .

10

In a wet scrubber, the water from the scrubber will react with the oxidation product of NO_x and dissolve the oxidation products removing them from the gaseous effluent. Preferably N_2O_5 will react with water to form nitric acid that will dissolve in the water. If an alkaline base is present in the water, a nitrate salt will be formed that can be used as fertilizer. The alkaline base however will also react with other acidic components in the gaseous effluent, causing larger amounts of side product to form. Therefore in a more preferred use, an acidic wet scrubber is used. The acidic medium will still absorb the higher nitrous oxides, but will not or less absorb the basic or weak acidic components present in the gaseous effluent, typically carbon dioxide. During the fertiliser production process large amount of CO_2 are produced and an alkaline scrubber would absorb these large amounts of CO_2 , using large volumes of scrubber solution and generating large amounts of waste products.

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In a preferred use, the medium used in the wet scrubber is reclaimed water, meaning water that have been used before. More preferably the water has been used to clean at least parts of the fertilizer production plant, preferably reactors, pipes or the floors of the plant. Salts and other components related to fertilizer production will be dissolved in said water. Most preferably, the reclaimed water is acidic.

30

In a third aspect according to the invention, a fertilizer production plant is provided, comprising:

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- a reactor;
- a gas outlet, connected to the reactor;
- a wet scrubber, configured to receive a NO_x -containing gaseous effluent produced in the reactor;
- a connector, connecting the gas outlet and the scrubber, configured to transport the gaseous effluent;

wherein an ozone generator is connected to the connector or the wet scrubber, configured to inject ozone into the gaseous effluent.

5 In a preferred embodiment of a fertilizer production plant according to the invention a gas analyser is present in the gas outlet, the connector or a final stack connected to said wet scrubber, and is configured to analyse at least part of the composition of the gaseous effluent and control the ozone injection on the basis of the NO_x concentration measured.

10 **DESCRIPTION OF FIGURES**

FIG. 1a shows a schematic representation of a batch digestion set-up of the digestion of phosphate rock with nitric acid according to the invention;

15 FIG. 1b shows the NO_2 emission during a batch digestion process of the digestion of phosphate rock with nitric acid;

FIG. 1c shows the influence of humidity in the batch digestion off-gases on the NO_2 ozonation for various molar ratios O_3 / NO_x ;

20 Figure 2 shows a schematic representation of an exemplary set-up of a fertilizer production plant applying the digestion of phosphate rock with nitric acid according to the invention;

25 FIG. 3a shows a schematic representation of an exemplary set of a pilot plant of the digestion of phosphate rock with nitric acid according to the invention;

FIG. 3b shows infrared spectra of the gaseous effluent before and after reaction with ozone and passing through the wet scrubber.

30 FIG. 3c shows the profile of the NO_2 -concentration during an experiments wherein the same residence time (RT) but an increasing O_3/NO_2 ratio is applied;

35 FIG. 3d shows the influence of the residence time of the reaction gases on the efficiency of the conversion of NO_2 ;

FIG. 3e shows a surface response plot of the pilot plant results with an initial NO_x amount of 397,8 ppm, wherein the NO₂-concentration in the flue gas outlet is plotted versus the residence time (RT) and the ozone inlet concentration (O₃ in).

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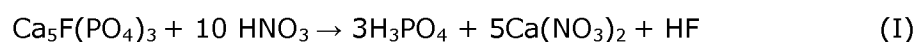
DETAILED DESCRIPTION OF THE INVENTION

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within that range, as well as the recited endpoints.

The invention relates to the removal of NO_x from gaseous effluent generated in fertilizer production, more preferably NPK fertilizer production, and most preferably acid digestion of phosphate ore, using ozone to treat the gaseous effluent, resulting in a resultant gas mixture, thereby oxidizing NO and NO₂ present in the NO_x to higher oxides, and furthermore using a wet scrubber through which the resultant gas mixture is passed, thereby removing the higher nitrogen oxides.

Acid digestion of phosphate ore, also called phosphate rock, is a well-known process in the production of fertilizers. Phosphate ore is treated with nitric acid. The process can be represented by reaction (I):



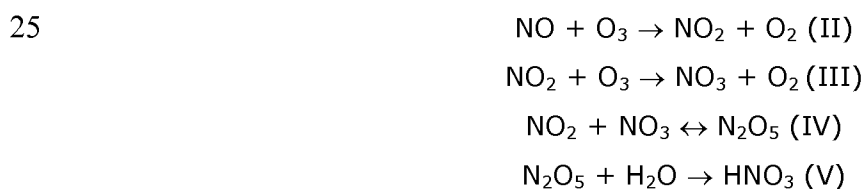
NO_x is released during this reaction as a main side product. And this NO_x has a composition with a high amount of NO₂, typically of 80 to 100 mole% NO₂ and 0 to 20 mole% NO, more preferably 90 to 95 mole % NO₂ and 5 to 10 mole % NO.

The treatment of phosphate rock with nitric acid as described above is the preferred process for the production of NP or NPK fertilizer, as in one reaction phosphate as well as nitrate salt are formed simultaneously. The main drawback is however the amounts of NO_x that are produced during this process. The use of sulphuric acid in the digestion of phosphate ore does not produce NO_x, but it produces one equivalent

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of gypsum, also referred to as phosphogypsum, as it comes from the digestion of phosphate ore. This phosphogypsum has economically no value, even more because of weakly radioactive nature of phosphogypsum special precautions need to be taken in the disposal of it and most of the time the phosphogypsum is landfilled. Hence again, the use of nitric acid for at least partially replacing sulphuric acid in the digestion of phosphate ore is preferred.

The NO_x of the gaseous effluent released during fertilizer production has a composition of preferably 80 to 100 mole% NO_2 and 0 to 20 mole% NO , more preferably 90 to 95 mole % NO_2 and 5 to 10 mole % NO , which is a different NO_x composition than other chemical processes where NO_x is released. For instance, combustion of fossil fuels in the presence of air produces a NO_x composition with large amounts of NO , up to 95 mole% NO , and small amounts of NO_2 , up to 5 mole%. Pickling metals also releases NO_x , but with a larger NO_2 amount, up to 35 - 40 mole% NO_2 and up to 60 - 65 mole% NO . In the production of nitric acid, the NO_x composition released comprises around 50 mole% NO and 50 mole% NO_2 . Hence, for the gaseous effluent released during fertilizer production with a NO_x composition of at least 80 mole% NO_2 , and other impurities preferably dust, droplets, hydrogen fluoride, silicon tetrafluoride and large amounts of water vapour, different reaction conditions are needed for an effective removal of NO_x from the gaseous effluent. Theoretically, $\frac{1}{2}$ mole of ozone is needed to convert one mole of NO_2 into N_2O_5 . The simplified mechanism of the process can be represented by the following reactions (II - V):



Hence, a NO_x composition with a high percentage NO_2 needs less ozone than a NO_x composition with a large fraction of NO . In practice, an excess of ozone is needed to obtain a satisfying conversion from NO_x to higher nitrogen oxides. These higher nitrogen oxides are more soluble and/or more reactive with water. Hence, these higher nitrogen oxides can be easily removed from the gaseous effluent with a wet scrubber.

Using a large excess of ozone, for example more than two equivalent, will oxidise all the NO_x present in the gaseous effluent, but the unreacted ozone needs to be

destroyed before the gaseous effluent can be released in the atmosphere, this because ozone is harmful to humans and other living organisms, affects the respiratory system and is a greenhouse gas itself. Ozone reacts with other compounds in the atmosphere and can form pollutants that can be more harmful than the ozone itself. Overall, using a large excess of ozone is not cost efficient, as resources and energy need to be used to produce ozone that largely will be destroyed without being used in a desired chemical reaction. The majority of the ozone produced is to push the oxidation reaction of NO_x to completion. This puts extra pressure on the environment as more resources and energy need to be used for as well production and destruction of ozone. Therefore, the amount of ozone needed to oxidise NO_x in the gaseous effluent needs to be optimised to make the whole removal process economical and environmentally viable.

The amount of excess ozone that is needed in practice compared to the theoretical amount can't be deduced from other NO_x compositions. The excess depends on other components present in the gaseous effluents, some of these components can be oxidised as well or interfere with the oxidation of NO_x . The amount of water vapour in the gaseous effluent, the amount of dust particles, the temperature of the gaseous effluent all have an impact on the speed and yield of the oxidation reaction. Furthermore, the composition of the gaseous effluent is not a constant, fluctuations in NO_x and other components can vary quite significantly during one process. Especially for batch processes, the composition of the gaseous effluent at the beginning of the process is completely different from the composition at the end of the process. Also, the removal of NO_x from the gaseous effluent needs to be robust, meaning that external factors preferably air humidity and external temperature don't disturb the efficacy of the removal process. Changes in external factors can't lower the efficacy of the removal of NO_x in the gaseous effluent under preferably 70 %, more preferably under 75 %, even more preferably under 80 % and most preferably under 85 %. Efficacy is expressed as the percentage of mole NO_x that has been removed from the gaseous effluent over the moles NO_x that were initially present.

The higher nitrogen oxide preferably is dinitrogen pentoxide or N_2O_5 . N_2O_5 reacts with water to form nitric acid, and is therefore removed from the gas phase as the nitric acid is dissolved by the water in the scrubber. N_2O_5 is the oxide of nitrogen with a fast reaction rate or high solubility (see table 1), and is therefore the most preferred oxide for fast removal of nitrogen oxides from a gaseous effluent.

Table 1 shows the different Henry's law constants for the different oxides from nitrogen. The Henry's law constant of a compound is proportional to the solubility of the compound. The Henry's law constant and thus the solubility of N₂O₅ is two orders of magnitude higher than the one of NO₂ and three orders of magnitude higher than the one of NO. The Henry's law constant of nitric acid or HNO₃ is extremely high compared to the ones of the oxides.

Nitrogen species	Henry's parameter
	Kmole.m ⁻³ .kPa ⁻¹
NO	1.87 · 10 ⁻⁵
NO ₂	1.18 · 10 ⁻⁴
NO ₃	3.36 · 10 ⁻⁴
N ₂ O ₃	5.92 · 10 ⁻⁴
N ₂ O ₄	1.38 · 10 ⁻²
N ₂ O ₅	2.07 · 10 ⁻²
HNO ₃	4.83 · 10 ^{+8.00}

Table 1: Henry's law Constants

The reaction of N₂O₅ with water is represented by reaction (V) as shown above.

10

The wet scrubber used in this process is preferably a scrubber using reclaimed water or a scrubber with an acidic medium.

The gaseous effluent preferably comprises at least one of the following list: sulphur oxides, water vapour, hydrogen fluoride, silicon tetrafluoride, nitric acid, carbon dioxide or dust.

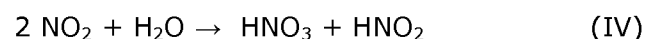
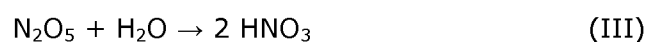
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Preferably, only one wet scrubber is used for the removal of NO_x from the gaseous effluent.

20

During the passage of the resultant gas mixture through the wet scrubber, preferably nitric acid is formed as shown in reaction (III). If any unreacted NO₂ is present at this stage, the NO₂ will form a mixture of nitrous and nitric acid as shown in reaction (IV).

25



The temperature applied in the treatment of the gaseous effluent comprising NO_x produced during fertilizer production with ozone preferably is 130 °C or less, more preferably 110 °C or less, even more preferably 100°C or less and most preferably 80 °C or less.

5

In order to measure the concentration of NO_x in the gaseous effluent, a gas analyser is provided to measure the concentration of NO_x in the gaseous effluent and regulates the amount of ozone added to the gaseous effluent in step a) on the basis of the NO_x concentration measured.

10

In the example provided in Fig. 2, a fertilizer production plant according to the invention is shown. This fertilizer production plant comprises:

- a reactor 1;
- a gas outlet 2, connected to the reactor 1;
- 15 - a wet scrubber 5, configured to receive a NO_x-containing gaseous effluent producible in the reactor 1;
- a connector 4, connecting the gas outlet 2 and the scrubber 5, configured to transport the gaseous effluent;

wherein an ozone generator 3 is connected to the connector 4 or the wet scrubber 5, configured to inject ozone into the gaseous effluent.

20

Preferably, a gaseous effluent that can be formed in the reactor 1 can only leave the reactor 1 via the gas outlet 2.

25 A connector 4 connects the gas outlet 2 to a wet scrubber 5 in a way that a gaseous effluent that can be formed inside the reactor 1 can reach a wet scrubber 5. Reactor 1 can be filled with reactants 11 needed in the fertilizer production process and is foreseen with an overflow 7, preventing reactants or reaction mixture to enter into the gas outlet 2.

30

An ozone generator 3 is connected to the connector 4, and this in a way that the ozone that can be generated by the ozone generator 3 can be injected into the connector 4 where the ozone can mix and react with the gaseous effluent that can travel through the connector 4.

35

The ozone generator 3 makes it possible to oxidise the NO_x to higher nitrogen oxides. The length of the connector 4 between where the ozone is injected 12 and the gas inlet 13 of the wet scrubber 5 determines together with the flow rate of the

gaseous effluent the reaction time or residence time. The time between the gaseous effluent being mixed with the ozone and the entry in the wet scrubber is. In other words, the resident time is the time between the gaseous effluent being mixed with the ozone and the entry in the wet scrubber. Preferably, the length of the connector 4 is designed such that the residence time is 0.5 to 15 seconds, preferably 3 to 15 seconds, more preferably 4 to 13 seconds, even more preferably 5 to 11 seconds, and typically 7 seconds. This way preferably 70 %, more preferably 80 %, even more preferably 90 % and most preferably 100 % of the NO_x are oxidised to a higher nitrogen oxide by the time the gaseous effluent reaches the wet scrubber 5.

The wet scrubber 5 makes it possible to remove the higher nitrogen oxides efficiently from the gaseous effluent as these higher nitrogen oxides have a high solubility in the scrubber medium 8 or react with the water in the scrubber medium 8 to form water soluble salts or acids. The scrubber medium 8 comprising the nitric acid or salt can leave the wet scrubber 5 via medium outlet 9. Fresh and/or reused scrubber medium 8 can be introduced in the wet scrubber 5 via medium inlet 10. Overall, with the fertilizer production plant from the invention nitric acid can be used for the production of fertilizer, and more preferably the digestion of phosphate ore with no or strongly reduced NO_x emissions. Preferably 70 %, more preferably 80 %, even more preferably 90 % and most preferably 100 % of the NO_x are removed from the gaseous effluent that is generated in fertilizer production and leaves the production plant via final stack 6.

Alternatively, the ozone generator 3 can be directly connected to the wet scrubber 5, and this in a way that the ozone generated by the ozone reactor can be injected in the wet scrubber 5 and mix there with the gaseous effluent. The oxidation will still work but the large amounts of water present in the scrubber will slow down the oxidation reaction.

Preferably, a gas analyser 14 is present in the gas outlet 2, the connector 4 or a final stack 6 connected to said wet scrubber 5, and is configured to analyse at least part of the composition of the gaseous effluent and control the ozone injection on the basis of the NO_x concentration measured.

The gas analyser 14 makes it possible that at least the concentration of NO_x is determined in the gaseous effluent that can be produced in the reactor 1. This information can be used to control the amount of ozone that is generated by the ozone generator 3 and is injected in the gaseous effluent. This way a predetermined ratio of ozone to NO_x can be maintained, and is always the right amount of ozone

present in the gaseous effluent and is less ozone wasted at point that the concentration of NO_x in the gaseous effluent drops.

5 The invention is further described by the following examples which illustrate the invention.

EXAMPLES

10 Experiments have been carried out both on laboratory scale as well as pilot scale for real flue gases (= off-gases) generated during the digestion process of phosphate rock with nitric acid. It is remarked that in the laboratory as well in the pilot plant tests, NO_2 as well as NO was measured. However, the concentration of NO was so low that it was considered as not relevant (see also figure 3b).

15 Example 1:

A first series of experiments were conducted on a laboratory scale for gases coming from a batch digestion process. A phosphate rock batch digestion process is by nature an unstable process. Therefore, stable periods of NO_x emission were observed and were chosen for the studying of NO_x ozonation.

20

In Figure 1a, a batch digestion of phosphate ore with nitric acid is shown. In a glass reactor, more specifically a three neck flask 21 with a flat bottom that is placed on a heatable plate 22, this plate 22 also covering a magnetic stirrer (not shown on the figure), the nitric acid and phosphate rock 23 in proportion of 370 cm^3 of 59 w/w% nitric acid and 200 g of phosphate rock were added and heated by means of the plate. By mixing the nitric acid and the phosphate rock by means of the magnetic stirrer, a mixture of nitric acid and phosphate rock was prepared in the three neck flask 21. Once the reaction had started, a flow of 5 dm^3/min air 24 was added to the three neck flask 21. To the resulting batch digestion off-gas 25, ozone (O_3) 26 was added. The ozone was produced by converting O_2 , stored in a oxygen gas cylinder 27, by means of an ozone generator 28 to O_3 . An ozone generator producing up to 10 g/h was used. The reaction between the ozone 26 and the resulting batch digestion off-gas 25 took place in an ozonation reactor 29 (in the form of a tube made out of an ozone resistant material). The produced gas stream 30 coming out of the ozonation reactor 29 was analysed using an FTIR (Fourier Transform Infrared) spectrometer 31, more specific a Gasmeter portable DX-4000, equipped with a gas cell with an optical path of 2.5 meter. The sampling line 32 was adjusted to a flow of 4,5

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30
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dm³/minute. Additionally, an escape outlet 33 for excess gas / surplus air was added to the set-up.

The temperature of the digestion process was controlled in the range of 60 to 70°C. For the magnetic stirrer, three mixing speeds were used, i.e. 200, 300 and 350 rpm. This enabled to obtain quasi-stable NO₂ concentrations in the gas phase around 130 and 250 ppm (in different batch tests). The residence time applied in this batch digestion experiment was around 5 seconds.

Figure 1b depicts the NO₂ emission during this batch digestion. The x-axis represents time since addition of nitric acid to the phosphate rock, expressed in minutes. The y-axis represents the concentration of NO₂ in the gaseous effluent, expressed in parts per million or ppm. It is clear that in the first 20 minutes, a much higher concentration of NO₂ is released than after 20 minutes. NO₂ emission stabilises from 20 minutes onwards. Even though the same reaction conditions were used for different batches (see different symbols on the figure), it can be seen that the concentration is still different for every batch.

Figure 1c depicts the influence of humidity in the batch digestion off-gases on the NO₂ ozonation for various molar ratios O₃ / NO_x. It was observed that the presence of water vapour in the batch digestion off-gases increased the NO₂ conversion rate. The influence of water vapour content was growing with the increasing molar ratio O₃/NO_x.

In table 2, the NO_x removal efficiency for the batch digestion process is shown. In this test, the digestion process parameters were arranged in a way to obtain different NO₂ concentrations (see the left column of table 2). Ozone was added to these different initial NO₂ concentrations. When starting the addition of O₃ to the batch digestion off-gas, the initial NO₂ concentration was measured. It was also known how much O₃ had been added to the batch digestion off-gas (by using a calibrated ozone generator). In this way, the molar ratio of O₃ versus NO_x could also be determined (see the middle column of table 2). Then, the obtained NO_x removal (see the right column of table 2) was determined by the formula:
(begin concentration of NO₂ * begin volume NO₂ - end concentration NO₂* end volume NO₂) / (begin concentration NO₂ * being volume NO₂)

Initial NO₂ concentration	Molar ratio O₃/NO_x	Obtained NO_x removal
ppm	mole/mole	%
140	0.5	43
190	0.8	50
138	1.1	83
145	1.7	100

Table 2: NO_x removal efficiency for the batch digestion process

Out of table 2, it can be deduced that a higher ratio of O₃/NO_x results in a better removal of NO_x.

5

Based on the digestion batch process, the preferred molar ratio of O₃/NO_x for complete removal of NO₂ is around 1.7 for a residence time of 5 seconds and an ambient temperature (between 22 and 25°C).

10 Example 2:

A second series of experiments were conducted for real flue gases from phosphate rock digestion pilot plant.

In figure 3a, a simplified pilot plant set-up is shown in which a continuous process is exerted. This pilot plant comprises two digestors 41 and 42 that are placed in series. The first digester 41 is mandatory. In this first digester 41, phosphate rock and nitric acid 45 are added. This first digester 41 is provided with a gas outlet 46 for letting out the pilot plant off-gases 46 formed by the reaction of the phosphate rock and the nitric acid. The second digester 42 is optionally and is to take care that there is sufficient residence time. This second digester 42 is connected to the first digester 41 via an overflow 43. This second digester 42 gives extra time for the reaction between nitric acid and phosphate rock that started in the first digester 41 to take place. The overflow 44 of the second digester 42 goes to a buffer (not shown on the figure). The pilot plant off-gases 46 coming from the first digester 41 are then directed to a venting line 47. In this venting line 47, ozone is added to the pilot plant off-gases 46 at insertion point 50. In this venting line 47, five measuring points P₀ – P₄ that are measured with an FTIR are installed, i.e.

- P₀ – measurement point for flue gas velocity;
- P₁ – before ozone injection (residence time 0 sec);
- P₂ – after ozone injection (residence time around 3 sec);
- P₃ – after ozone injection (residence time around 7 sec); and
- P₄ - after ozone injection (residence time around 10 sec).

30

The venting line 47 has a length of about 100 meters. Between each two measuring points $P_1 - P_4$, 25 meters of venting line 47 is provided.

5 The used ozone generation equipment 47 consists mainly of an oxygen generator, an ozone generator (OZAT CFS-7 2G - nominal O_3 production from O_2 up to 500 g/h) and a control system (not shown in the figure). After the last measuring point P_4 , the gas stream is then directed to a wet scrubber 51. The wet scrubber 51 comprises a scrubber medium, preferably water, that enters the wet scrubber 51 via a medium
10 inlet 54 and that leaves the wet scrubber 51 via a medium outlet 53. The purified pilot plant off-gases leave the scrubber via the outlet 52.

The total flue gases flow rate was kept between 49-73 m^3/h . The flow rate of the oxygen-ozone mixture stream was equal to 2 m^3/h . The ozone-oxygen mixture was
15 injected through a Venturi mixer (Mazzei Injector Company) (0.5 m after the first measuring point P_1). An HACH Indigo Method No. 8311 using AccuVac Ampuls was used to analyze residual ozone concentration in the reaction gases.

Series of experiments were conducted for real off-gases from a phosphate rock
20 digestion process. The digestion process parameters were arranged in a way to obtain NO_2 -concentration around 400 ppm. Different flow rates as well as different sampling points were used in order to verify ozonation process efficiency for various residence times. The flue gases from the reactor were vented into the absorption columns that are part of the pilot plant (not shown on the figures).

25 During the tests, the NO_x levels in the pilot plant off-gases varied between 240 and 450 ppm. The temperature of the pilot plant off-gases varied between 25 – 40°C. The molar ratio of ozone that was applied was varied between 0.26 and 1.35 O_3/NO_2 .

30

In table3, the results of the pilot plants tests are shown:

No	NO ₂ in	O ₃	R _t	T	MR	NO ₂ out	Red
	ppm	ppm	s	°C	-	ppm	%
1	453.7	246.78	4.00	37.30	0.54	120.40	73
2	420.8	231.41	7.41	37.30	0.55	82.70	80
3	370.9	173.47	11.45	37.30	0.47	111.10	70
4	433.93	407.89	2.70	27.70	0.94	63.65	85
5	403.55	375.30	5.40	27.70	0.93	40.00	90
6	341.91	150.44	3.14	26.10	0.44	203.65	40
7	341.91	218.82	3.14	26.10	0.64	135.32	60
8	240.86	325.16	3.14	26.10	1.35	1039	96
9	270.24	227.00	3.14	26.10	0.84	22.91	92
10	293.17	74.96	3.35	35.00	0.26	228.01	22
11	291.26	152.12	3.35	35.00	0.52	173.76	40
12	291.26	207.44	3.35	35.00	0.71	168.20	42
13	274.65	244.51	3.35	35.00	0.89	123.91	55
14	316.75	337.80	3.23	35.00	1.07	25.08	92
15	316.75	379.43	3.23	35.00	1.20	1.11	1000
16	288.48	78.55	6.80	39.80	0.27	261.70	9
17	292.91	150.46	7.19	39.80	0.51	203.08	31
18	309.85	97.53	6.89	39.80	0.31	232.99	25
19	309.85	138.17	6.89	39.80	0.45	192.26	38
20	277.96	218.31	6.89	39.80	0.79	142.48	49
21	277.96	324.97	6.89	39.80	1.17	66.32	76
22	277.96	221.09	6.89	39.80	0.80	78.94	72
23	277.96	288.86	6.89	39.80	1.04	9.34	97

Table 3: Test results collected from pilot plant tests

5

It was observed that in the pilot plant tests, the reaction progressed faster than in the lab tests. After 4 seconds, the ozonation reaction already was complete. For the complete removal of NO_x, an excess of ozone was required. No ozone could be detected in the gas samples taken after 4 seconds residence time which suggests that the excess of ozone must have decomposed.

10

Figure 3b depicts an example of the infrared spectra of the gaseous effluent before and after reaction with ozone and passing through the wet scrubber selected from one of the conducted experiments. The absorbance band of NO₂ at 1628 cm⁻¹ is absent in the gaseous effluent after treatment with ozone. Since nitric oxide is

15

present in the gases only in concentrations as low as 5 ppm, in order to verify the effectiveness of ozonation processes, only the analysis of the NO₂ concentrations is done. The CO₂ peaks have a similar surface area before and after the addition of ozone, this indicates that the changes observed are not due to dilution of the gas mixture. Apart from NO and NO₂, the FTIR analyser enabled also to measure concentrations of other gas components like H₂O, CO₂, CO, N₂O, SO₂, NH₃, HCl, Hf, SiF₄ and HNO₃. In this figure 3b, it can be observed that for all the measured gas components, except for NO₂, NO and HNO₃, there is no influence of the ozonation process on their concentrations. It can therefore be concluded that they do not react with ozone.

Figure 3c shows the results of a series of experiments wherein the same residence time (RT) of 3 seconds is applied but an increasing O₃/NO₂ ratio (0.44, 0.64, 0.95). Some variation in NO₂-concentration was observed during ozonation of the real flue gases (= off-gases). A few peaks can be observed that correspond well with the times when an antifoaming agent is added to the digestion process (in a normal operation procedure). The figure 3c shows measured NO₂-concentrations before and during ozonation for an average NO₂-concentration of 341.9 ppm. Out of this figure 3c, it can be deduced that NO₂ removal efficiency rises with increasing O₃/NO₂ ratio from 40.4 to 97%.

In order to analyse the ozonation process in a wider range of O₃/NO₂ ratio (0.2 – 1), two additional series of experiments were performed with different retention times, i.e. 3 and 7 seconds. In figure 3d, the influence of the residence time of the reaction gases on the NO₂-conversion efficiency is shown. For under-stoichiometric ratios O₃/NO₂ (0.2 and 0.3), the conversion degree was low as expected for both RTs. For stoichiometric O₃/NO₂ ratios around 0.5, the conversion was around 66%. Further increasing the molecular ratio to around 1 yielded almost to 100% NO₂ removal. Better results were obtained for longer residence times, here 7 seconds.

Figure 3e shows surface response plot with an initial NO_x amount of 397,8 ppm. Therein, the NO₂-concentration in the flue gas outlet is plotted versus the residence time (RT) and the ozone inlet concentration (O_{3_in}). Out of this figure 3e, it can be observed that the increase of the RT results in a growth of the degree of removal of NO₂.

Out of the pilot plant tests, it is clear that effectiveness of NO₂ removal from ozonated flue gases is dependent on the amount of ozone added, more precisely on

the molar ratio of ozone to nitrogen dioxide (NO_2). While the reaction stoichiometry expects a molar ratio of O_3/NO_2 equal to 0.5, the pilot plant test results showed that to obtain a substantially complete removal of NO_2 from the flue gases, the molar ratio O_3/NO_2 optimally is around 1. It is therewith emphasized that in the off-gases from phosphate rock digestion, many reactions are possible, e.g. ozone decomposition due to presence of water and dust and N_2O_5 reverse reaction or a possible ozone reaction with gas impurities, etc. These factors increase the required O_3/NO_2 ratio. On the other hand, tests have shown that the presence of water enhances the N_2O_5 removal from the off-gases by N_2O_5 absorption into the water, decreasing the required O_3/NO_2 ratio. Therefore, high humidity of real off-gases are beneficial for the process. Also the residence time is an important parameter of the reaction process. An increasing residence time allows the use of lower O_3/NO_2 for complete NO_2 removal.

In the pilot plant studies, a residence time around 7 seconds is sufficient for almost 100% NO_2 -conversion with a preferred molar ratio O_3/NO_2 of around 1.

Example 3

Different ozonation tests were performed to determine the NO_x efficiency for different molar ratios of ozone over NO_x . In table 4, the parameters of these different ozonation tests that were performed are shown, i.e. the ozone concentration added to the pilot plant off-gases, the ozone stream flow, the molar ratio of ozone/ NO_x and the residence time. The last column of table 4 shows the efficacy of oxidation depending on the molar ratio of ozone over NO_x present in a gaseous effluence expressed in percentage. As can be seen in the table 4 below, the residence time used in these trials varied around 5 seconds.

Ozone concentration (g/m ³)	Ozone stream flow (dm ³ /min)	Ozone/NO _x molar ratio	Residence time (s)	Oxidation efficacy
2.5	0.3	0.49	5.0	15 %
2.5	0.3	0.50	5.5	43 %
4	2	0.52	3.9	56 %
3	0.5	0.76	4.9	50 %
2.5	0.4	1.01	4.9	81 %
5	0.3	1.08	5.5	83 %
5	0.5	1.63	4.9	100 %
2.4	1	1.83	4.5	83 %
5	0.4	2.01	5.5	100 %
9.4	0.3	2.10	5.5	100 %
3	1	2.20	4.5	100 %
6	0.5	4.07	4.5	100 %
15	0.5	4.67	4.9	100 %
17	1	17.28	4.5	89 %

Table 4: NO_x oxidation efficacy for different molar ratios of ozone over NO_x

CLAIMS

1. A process for removal of NO_x from a gaseous effluent generated in the production of fertilizer, comprising the steps of:
 - 5 a) contacting the gaseous effluent with 0.7 to 1.4 equivalents ozone to every 1 equivalent of NO_x present in said gaseous effluent for 3 to 15 seconds, providing in a resultant gas mixture wherein NO and NO_2 present in the NO_x are oxidized to higher nitrogen oxides; and,
 - 10 b) passing the resultant gas mixture through a wet scrubber thereby removing the higher nitrogen oxides,wherein the gaseous effluent generated in the production of fertilizer has a NO_x composition of 80 to 100 mole% NO_2 and 0 to 20 mole% NO .
- 15 2. Process according to any one of previous claims, wherein the fertilizer production is by acid digestion of phosphate ore.
3. Process according to any one of previous claims, wherein the higher nitrogen oxide is N_2O_5 .
- 20 4. Process according to any one of previous claims, wherein the wet scrubber is an aqueous acidic scrubber.
- 25 5. Process according to any one of previous claims, wherein the gaseous effluent comprises at least one of the following list: sulphur oxides, water vapour, hydrogen fluoride, silicon tetrafluoride, nitric acid, carbon dioxide or dust.
- 30 6. Process according to any one of previous claims, wherein the scrubber in step b) is the only scrubber used for the removal of NO_x from the gaseous effluent.

7. Process according to any one of previous claims, wherein nitric acid or a salt thereof is formed in step b).
8. Process according to any one of previous claims, wherein the temperature in step a) is 130 °C or less.
9. Process according to any one of previous claims, wherein a gas analyser measures the concentration of NO_x in the gaseous effluent and regulates the amount of ozone added to the gaseous effluent in step a) on the basis of the NO_x concentration measured.
10. Use of ozone as an oxidant in the removal of NO_x from gaseous effluents generated in fertilizer production, wherein the gaseous effluent generated in the production of fertilizer has a NO_x composition of 80 to 100 mole% NO₂ and 0 to 20 mole% NO.
11. Use according to claim 10, wherein NO_x is removed from a gaseous effluent generated in the fertilizer production by means of oxidation by ozone of NO and NO₂ present in the NO_x to higher nitrogen oxides providing in a resultant gas mixture, and scrubbing the resultant gas mixture by means of a wet scrubber thereby removing the higher nitrogen oxides.
12. Use according to claim 10 or 11, wherein the fertilizer production is by acid digestion of phosphate ore.
13. Use according to any of claims 10 to 12, wherein ozone is used in a molar ratio of ozone over NO_x in the gaseous effluent of 0.7 to 1.4.
14. Fertilizer production plant comprising:
- a reactor (1) for acid digestion of phosphate ore;
 - a gas outlet (2) connected to the reactor (1);

- a wet scrubber (5) configured to receive an NO_x-containing gaseous effluent produced in the reactor (1);
- a connector (4), connecting the gas outlet (2) and the scrubber (5), configured to transport the gaseous effluent;

5 **characterised in that** an ozone generator (3) is connected to the connector (4) or the wet scrubber (5) and is configured to inject ozone into the gaseous effluent.

10 15. Fertilizer production plant according to claim 14, wherein a gas analyser (14) is present in the gas outlet (2), the connector (4) or a final stack (6) connected to said wet scrubber (5), and is configured to analyse at least part of the composition of the gaseous effluent and control the ozone injection on the basis of the NO_x concentration measured.

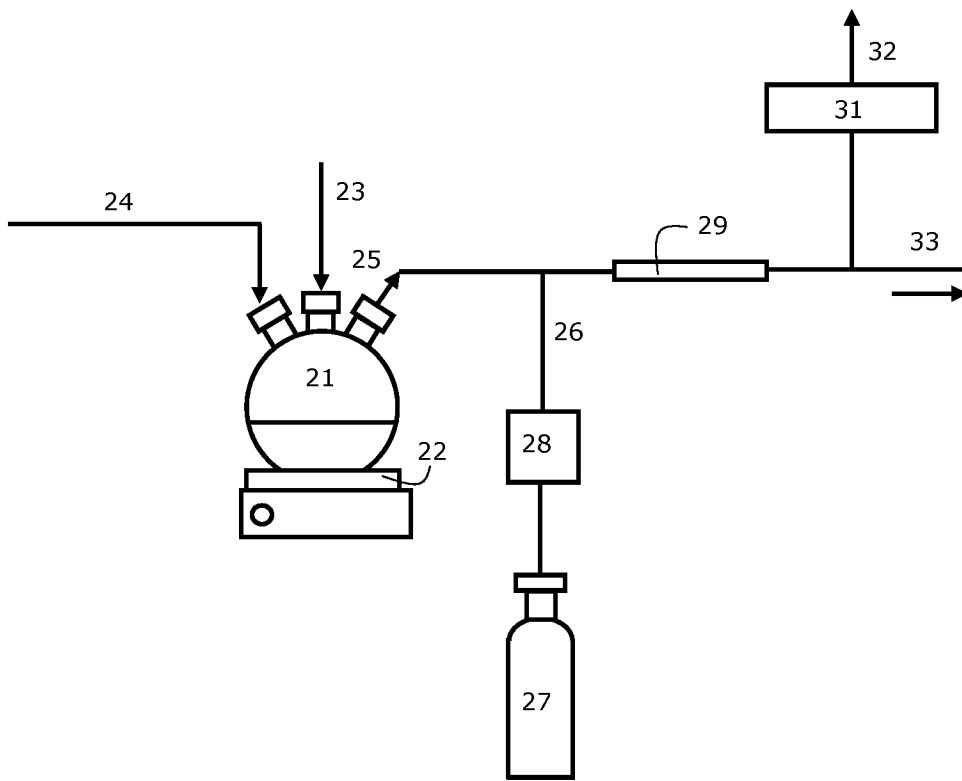


FIG. 1a

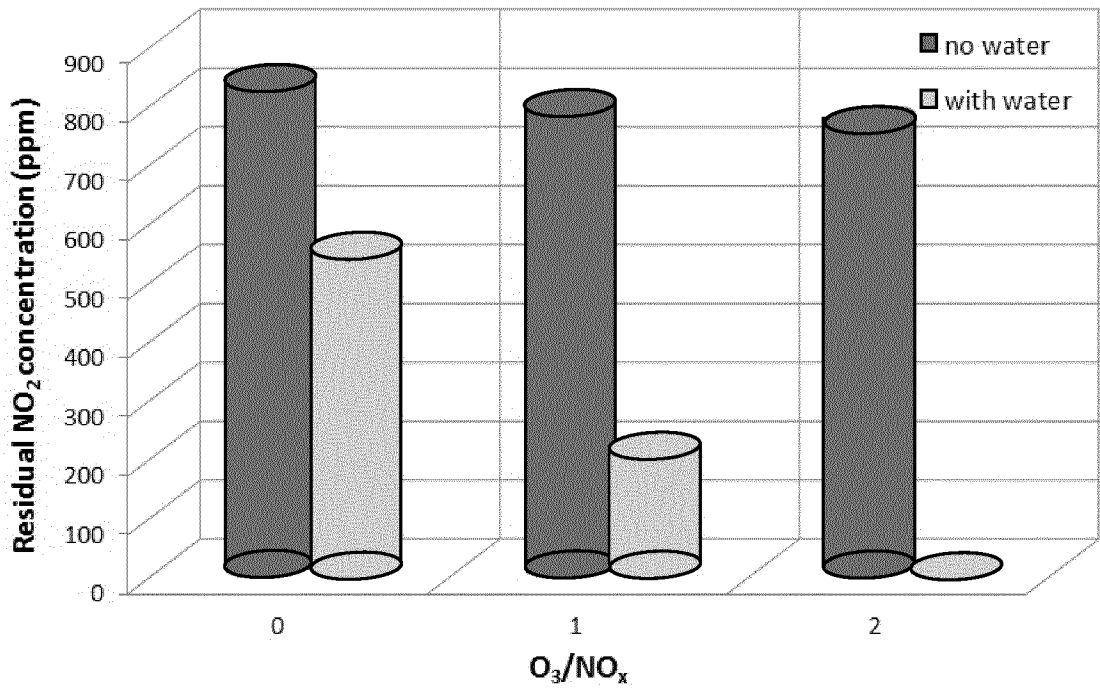


FIG. 1c

NO2 emission from batch digestion process



FIG. 1b

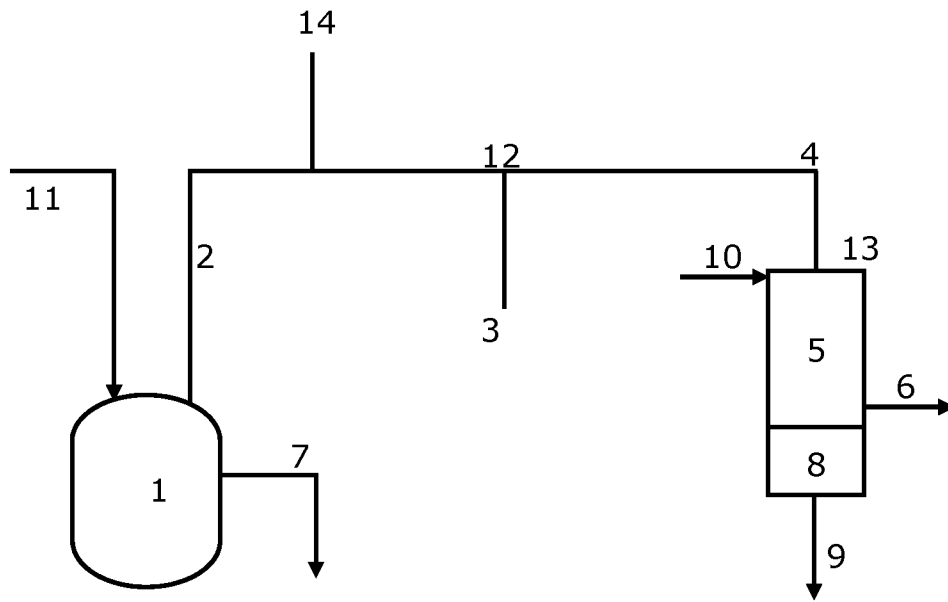


FIG. 2

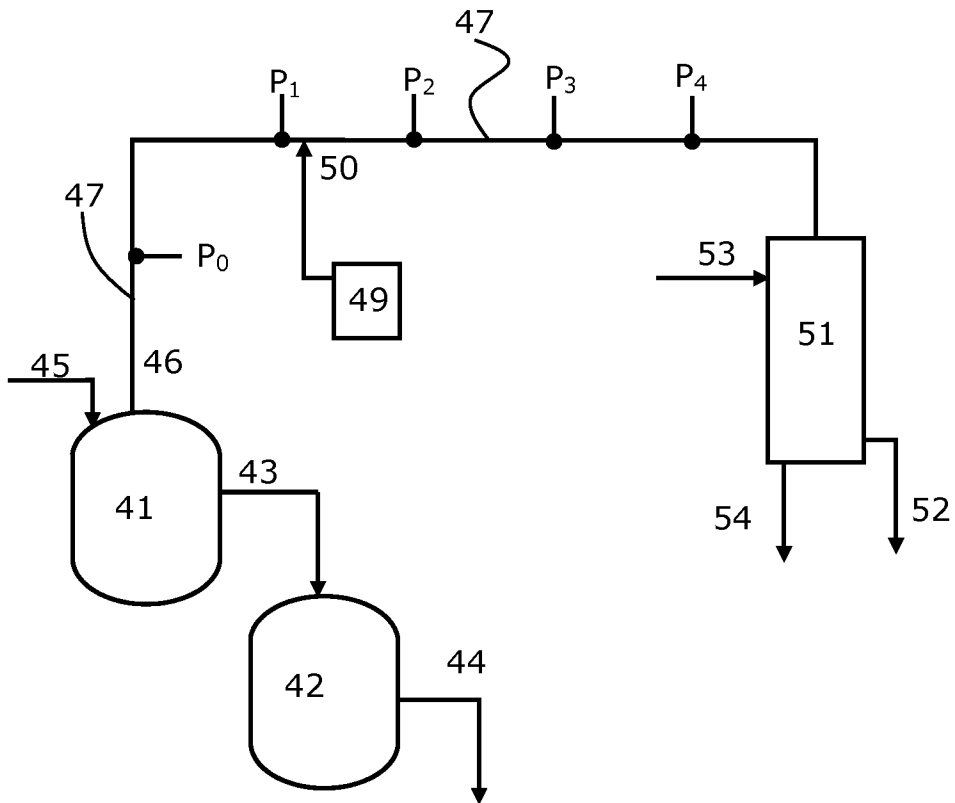


FIG. 3a

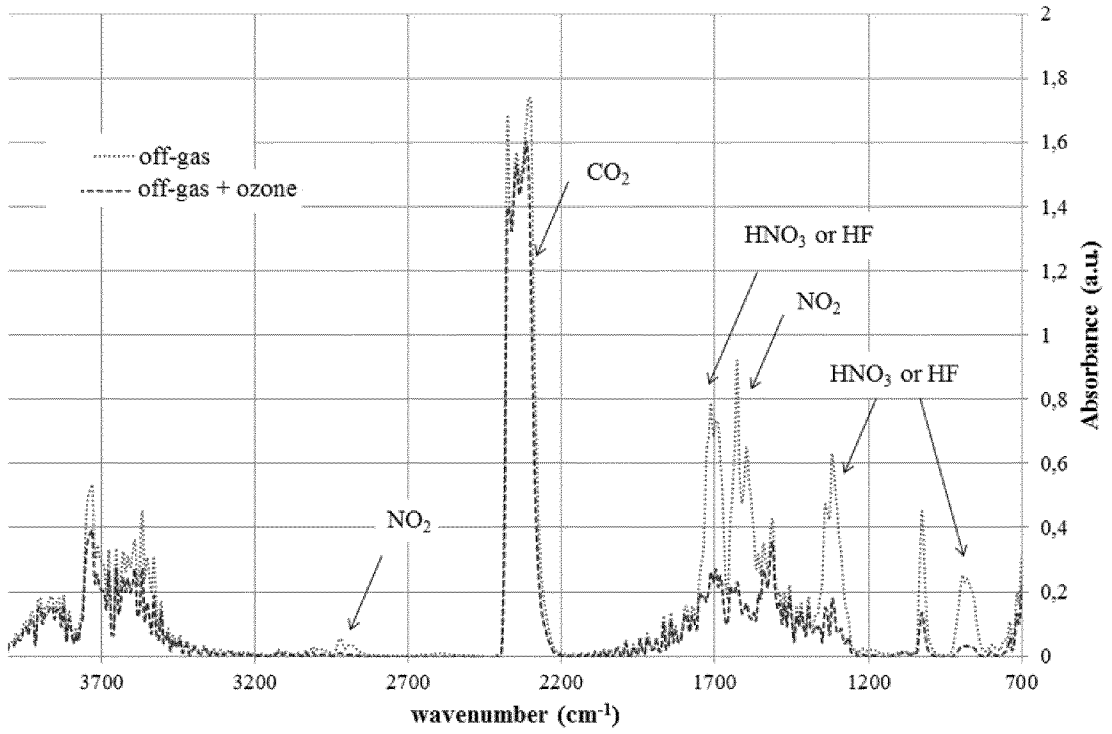


FIG. 3b

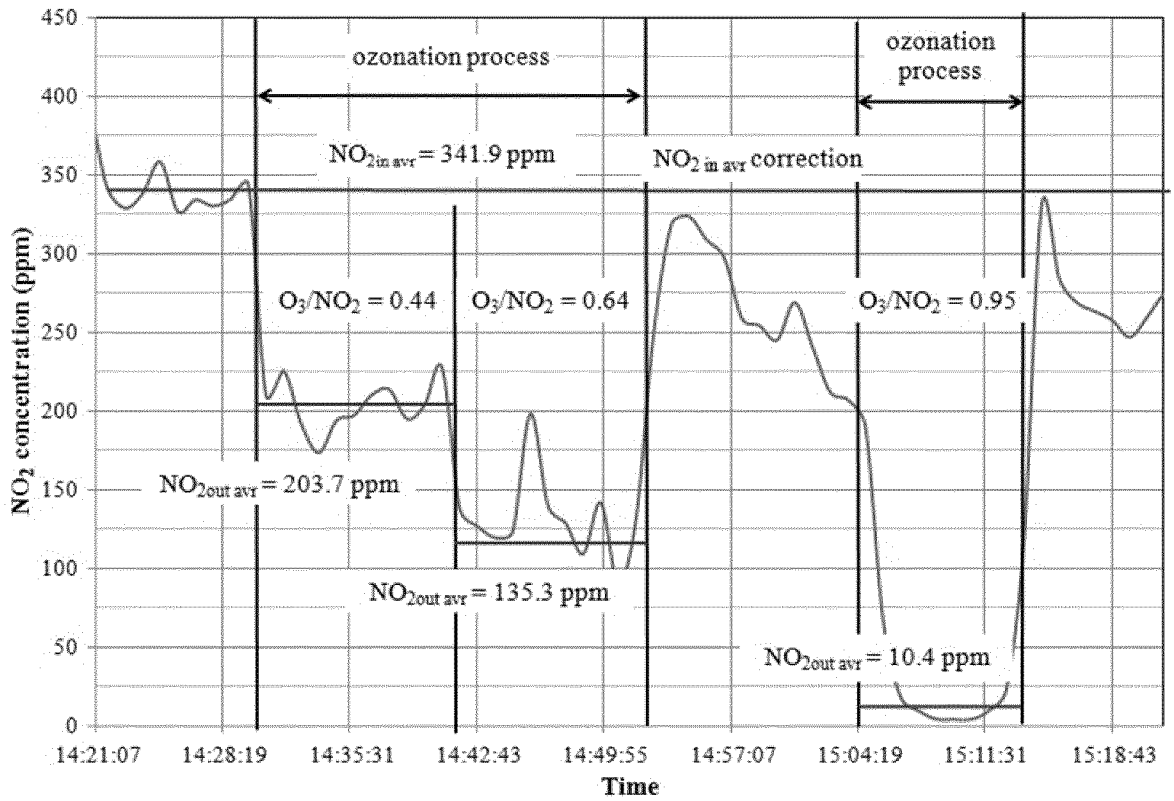


FIG. 3c

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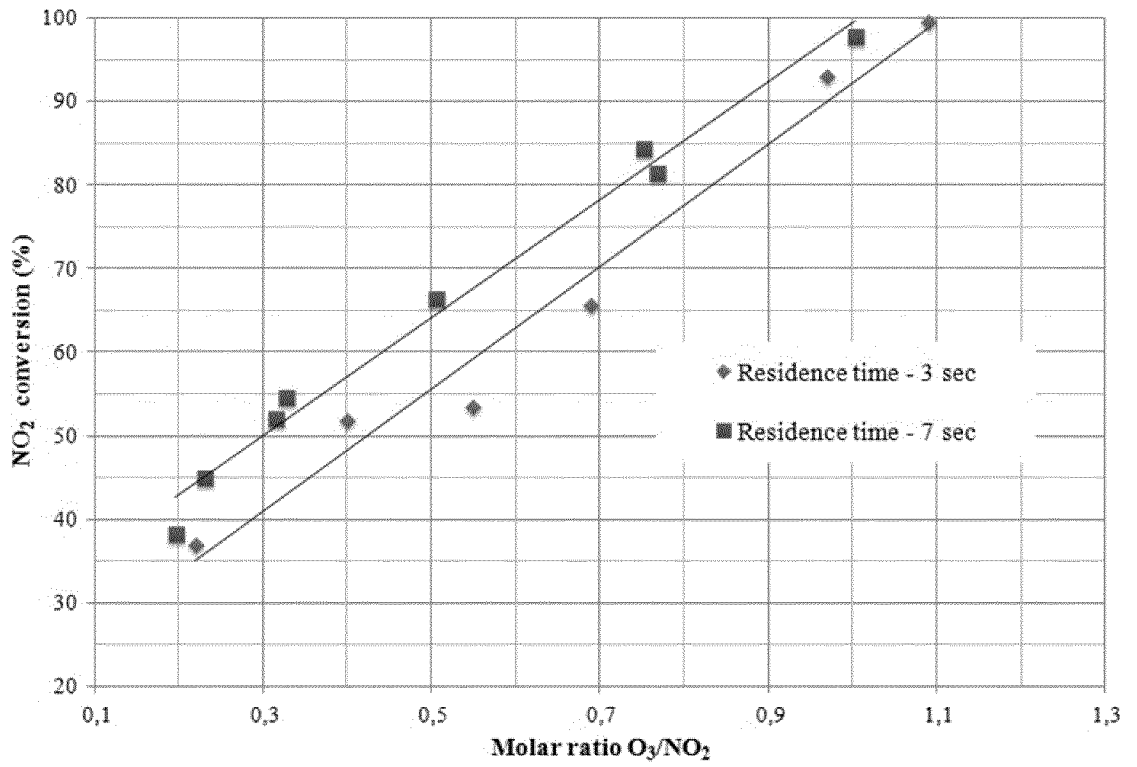


FIG. 3d

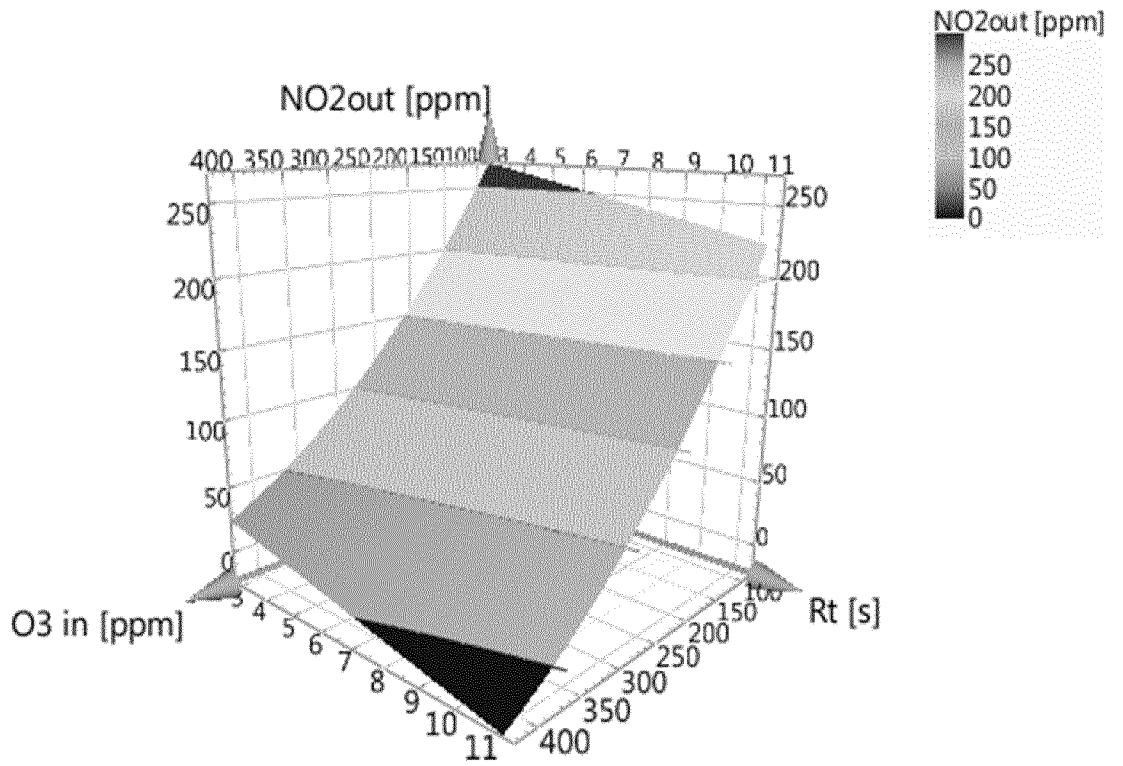


FIG. 3e

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059892

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/54 C05B11/06 B01D53/14
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B01D C05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 351 613 A2 (BASF AG [DE]) 24 January 1990 (1990-01-24) figure 1 claim 1 column 1, line 1 - line 15 -----	1-15
X	US 2005/084436 A1 (SUCHAK NARESH J [US] ET AL) 21 April 2005 (2005-04-21) paragraphs [0002] - [0004], [0007], [0017], [0049], [0059]; figure 1 -----	1-15
Y		1-15
A	EP 1 040 863 A2 (CANNON TECHNOLOGY INC [US]) 4 October 2000 (2000-10-04) cited in the application paragraph [0030] - paragraph [0032] -----	1-15
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search 1 August 2016	Date of mailing of the international search report 16/08/2016
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INTERNATIONAL SEARCH REPORT

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