

PROCESS FOR PLASMACHEMICAL CONVERSION OF N_2O into NO_x
AND/OR INTO ITS DERIVATIVES

The field of the present invention is that of the treatment and of the reclaiming of nitrous oxide
5 N_2O (laughing gas) and, more particularly its conversion into a product of the NO_x type with $x = 1$ or 2, and into derivatives, such as, for example, nitric acid HNO_3 .

The present invention relates to a process
10 for plasmachemical oxidation of dinitrogen oxide.

Out of a volume of 100 of N_2O discharged into the atmosphere, it is generally accepted that 70 % originates from the metabolism of the plant kingdom, 10 % from burning of all kinds, 10 % from motor vehicle
15 internal combustion engines and the remaining 10 % is gaseous industrial effluents. The source of 2 % of these effluents is the production of nitric acid and 8 % the production of adipic acid (one of the components on which polyamide 6.6. is based). (Cf. 5th
20 International Workshop on nitrous oxide emissions - July 1-3, 1992 Tsukuba [JP]).

For some time now, this nitrous oxide N_2O has given rise to considerable research efforts and large expenditure because it has been submitted that its
25 accumulation in the atmosphere may constitute a hazard to the environment. In particular, N_2O is suspected of contributing to the greenhouse effect phenomenon.



The lifetime of N_2O in the atmosphere is of the order of 170 years. It is a gas which is stable at ambient temperature and which practically does not combine with molecular oxygen and which stands up well to the action of conventional oxidizing agents.

The usual three main routes for the treatment or reclaiming of N_2O are:

- 1 - thermal destruction by burning,
- 2 - catalytic decomposition to gaseous nitrogen and oxygen N_2 and O_2 , and
- 3 - thermal conversion into NO_x with $x = 1$ or 2 and into its derivatives.

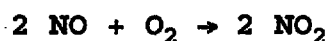
The third route is particularly advantageous because the NO_x compounds can be recycled, for example as nitric acid HNO_3 . The reclaiming of N_2O as HNO_3 is of the greatest interest, especially for the producers of adipic acid, given that nitric acid is employed for converting cyclohexanol and/or cyclohexanone, by oxidation, into adipic acid, this reaction furthermore producing approximately one mole of N_2O per mole of final adipic acid. (Nylon Production: an Unknown Source of Atmospheric Nitrous Oxide - N.H. Thiemens, W.C. Trogler, Science, Feb. 1991)

For this recycling to be viable it is absolutely essential that the conversion of N_2O into NO_x should be carried out in an economically profitable manner, that is to say with small quantities of energy, of reactants and of catalysts.



It is found, however, that the reaction N_2O giving $NO + \frac{1}{2} N_2$ is in competition with the reaction N_2O giving $N_2 + \frac{1}{2} O_2$.

The conversion of N_2O into NO_x is therefore
5 very tricky to implement, as illustrated by
Patent JP 61 25 79 40, which relates to a process for
the preparation of dicarboxylic acids in which a
recycling of nitric acid is employed. According to
this process the gaseous by-products of the nitric acid
10 oxidation of cyclohexanol and/or cyclohexanone to
adipic acid are continuously subjected to a thermal
decomposition without catalyst of N_2O into NO_x . The
latter is then converted into nitric acid by oxidation
and absorption in water, according to the following
15 reaction scheme:



The HNO_3 is then recycled into the adipic
acid synthesis reaction.

20 According to this Japanese patent the gaseous
by-products $NO + NO_2$, which are factors that limit the
conversion of N_2O into NO_x , must be removed as fully as
possible.

The content of the initial NO_x must be lower
25 than 10 % and, preferably, lower than 5 %.

The reaction temperature is between 1000 and
1300°C and preferably 1000 to 1200°C, and the residence
time from 10^{-2} to 100 seconds and, preferably from 10^{-1}



to 10 seconds. The gas to be treated is preheated with the aid of a heating device using hot air, of the heat exchanger type. The increase in temperature of the gas in the reactor is provided and self-maintained by the heat of decomposition.

The use of such temperatures is never a convenient operation and is a burden on the operating cost of the process.

From the examples in this patent it follows that the best result obtained is an efficiency of conversion of N_2O into NO of 25.4 %.

In these conditions this is generally insufficient to make the process economically attractive.

Scientific literature on the subject confirms this and teaches that the formation of NO and/or NO_2 represents, at most, only a few % of the N_2O converted (cf. especially A. A. Borisov, Kinet. Katal., 1968, 9 (3) 482 - W. H. Lipkea et al., Combustion Science and Technology, 1973, 6, 257 - Monat et al., Combustion Science and Technology, 1977, 16, 21 - I. S. Zaslonko et al., Kinet. Katal., 1980, 21, 311).

The unavoidable conclusion is therefore that the thermal decomposition of N_2O to NO_x and/or to its derivatives is not at present sufficiently efficient to be economically valid on an industrial scale, even though it is the most seductive route to reclaiming.

In this state of the art one of the essential



objectives of the present invention is to provide a process for converting N_2O into NO_x with $x = 1$ or 2 and/or into its derivatives, characterized by an NO_x production yield higher than 30 % mole/mole, in relation to the N_2O converted.

Another objective of the invention is to provide a process for thermal conversion of N_2O into NO_x ($x = 1$ or 2) and into its derivatives, which is easy to implement and, in particular, which does not require the reaction vessel to be brought to high temperature.

Another objective of the invention is to provide a process for converting N_2O into an NO_x derivative, for example of the nitric acid type.

Another objective of the invention is to provide a device for carrying out the process aimed at above, which contributes to reaching the objectives established above for the said process.

Thus, after numerous experiments and investigations, the Applicant Company has been credited with demonstrating that it was appropriate to make use of electrical arcs and/or discharges for the conversion of N_2O into NO_x with high yields of NO_x in relation to the N_2O converted.

As a result, the above objectives have been obtained by the present invention, which relates to a process for thermal conversion of N_2O into NO_x ($x = 1$ or 2), and/or into its derivatives, in which the N_2O is brought into contact with at least one electrical arc



and/or discharge.

More precisely, the process according to the invention consists:

- in forming a jet of gas to be treated comprising the N_2O ,
- in directing this jet into the interstitial space of at least two divergent electrodes to which electrical voltage is applied, so as to create at least one electrical arc and/or discharge and belonging to a low-temperature plasma generator, the latter operating by forming sliding electrical discharges between the electrodes, that the gas travels along the electrodes from the arc and/or discharge zone where the electrodes are closest to each other,
- and in recovering the gas comprising the NO_x formed.

Such a process offers the possibility of initiating the reclaiming decomposition of N_2O at low (ambient) temperature, outside thermodynamic equilibria. This is made possible by sliding electrical arcs and/or discharges which supply energy to the gas comprising the N_2O to be converted and which make it possible for reactive species to be generated outside thermodynamic equilibrium, the said species inducing exothermic reactions.

The NO_x yields obtained are higher than or equal to 30 % mole/mole, and this is markedly above the generally accepted limits, namely 25 % mole/mole.



This result is obtained at a low cost and with great flexibility and convenience in use.

The present invention would be incomplete if it did not include a device for implementing this process, this device comprising a reactor consisting of an adiabatic enclosure containing:

- a low-temperature plasma generator operating by formation of arcs and/or of sliding electrical discharges, and
- means for forming the gas jet.

This generator comprises at least one, preferably at least three pair(s) of divergent electrodes connected to electrical supply means and arranged so that they define an interstitial space forming a widening discharge zone.

The invention will be understood better and some of its other advantages and alternative forms of implementation will emerge clearly from the description which follows, of a nonlimiting example of embodiment of a device and of the process associated therewith, for plasmachemical conversion of N_2O into NO_x with $x = 1$ or 2 , with reference to the attached drawing in which the single figure shows, in lengthwise section, a basic diagram of a reactor forming the subject of the invention.

In this figure the reactor is indicated by the general reference 1. It comprises an adiabatic enclosure 2 containing means 3 for injecting the gas to



be converted, a plasma generator with sliding arcs and/or discharges 4, a tubular insert 5 for confining the gas and a zone 6 of conversion of the N_2O into NO_x .

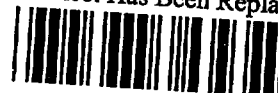
The means 3 for injecting the gas to be treated include a member 7 enabling the gas to be preheated if needed. This preheating member 7 (burner, electrical resistance, heat exchanger) is mounted on a conduit 8 for delivering the gas under entry pressure E to an injection nozzle 9 fitted into the cover 21 of the enclosure 2.

The nozzle 9 emerges at the base of six divergent electrodes 10a to 10f. They are conductive plates arranged in radial planes with an angular spacing of 60° , paired off and symmetrical in relation to the axes. These electrodes are divergent, that is to say that their facing inner faces diverge gradually from the base as far as their free ends.

These electrodes 10a to 10f define an interstitial space or a widening discharge and/or arc zone 11 in which the sliding electrical discharges and/or arcs are intended to move from the base towards the end of the electrodes.

The electricity supply to the electrodes is ensured by three-phase generators 12, represented symbolically with their connecting wires 13 on the drawing.

For further details reference will be made to the description of the plasma generator given by French



Patent Application No. 2 639 172.

The tubular insert 5 is coaxial with the enclosure 2 and smaller in height than the latter. The insert 5 defines with the bottom 2₂ of the enclosure 2 a space 14 for confining the gas entering under pressure through the nozzle 9. In the upper part, this space is occupied by the electrodes 10a to 10f.

Furthermore, insert 5 defines with the wall 2₃ of the enclosure 2 an outer annular chamber 15. The latter communicates with the interior of the insert 5 at the head of the enclosure and, at its base, comprises openings 16 connected to the conduits 17 for discharging the treated gas to the outside. A proportion of the gas arriving in this place can be recycled by means of a conduit 18 connecting the discharge conduit 17 to the delivery conduit 8. The circulation of the gas inside this conduit 18 is controlled by a pump 19 which can also be a part of the nozzle 9.

It is completely possible to envisage associating a module for converting NO_x into its derivatives, of the nitric acid type, with this device, by integration or in a manner which is independent and separate from the reactor for converting N₂O into NO.

This module may, for example, comprise means for cooling the gases leaving the conversion, and means of conversion in the strict sense.

A water-quenching system constitutes an



advantageous example of cooling means, especially since it makes it possible to avoid the decomposition of NO_x [sic] by a reverse mechanism of Zeldovich type.

The means of conversion preferably consist of an oxydoabsorption system, preferably of an oxydoabsorption column containing water.

As an alternative form of the device it would be possible to envisage including a so-called "plug" elongate adiabatic chamber in the reactor, so as to optimize the conversion of N_2O into NO_x .

In accordance with a preferred characteristic of the invention the materials of which the reactor and/or the electrodes consist are ceramics.

In operation, such an arrangement of the reactor 1 has the effect of causing the propulsion of the gas entering under pressure via the nozzle 9, from the bottom 2₂ of the confining space 14 towards the upper part including the electrodes 10a to 10f.

A turbulent regime is thus formed in the space 14 and more particularly in the arc and/or discharge zone 11, and this could also be called a turbulence zone.

The propelled gas then moves, under pressure, into the outer annular chamber 15 via the open upper end of the insert 5.

The gas is next conveyed towards the exit by travelling through the openings 16 of the discharge conduits 17.



The zone 6 for plasmachemical conversion of N_2O into NO_x is situated partly in the confining space, especially in the lower part of the latter, and partly in the zone 11 of the electrodes 10a to 10f and in the
5 outer annular chamber 15.

As far as the process for plasmachemical conversion of N_2O into NO_x and/or into its derivatives is concerned, it should be reported that it is preferable to implement it at a pressure of between 0
10 and 10×10^5 Pa, preferably between 0 and 6×10^5 Pa and, still more preferably, at a normal atmospheric pressure (1×10^5 Pa).

The gas to be converted consists of pure or substantially pure N_2O or alternatively of a mixture of
15 N_2O with air or N_2 and/or O_2 and/or CO_2 and/or NO and/or NO_2 or any other gas which is suitable for forming a dispersive gaseous medium for N_2O . It is important that the NO_x content of the gas to be converted should be lower than 10 % by volume, preferably lower than 5 %
20 by volume.

The gaseous mixture to be treated may, for example, be a residue of nitrous vapours obtained by the water treatment of the gases originating from the nitric oxidation of cyclohexanone and/or cyclohexanol
25 during the formation of adipic acid.

In addition, the Applicant Company has been able to demonstrate that it is particularly advantageous to remove water vapour from the gaseous



mixture containing the N_2O to be converted.

Any suitable and appropriate means is employed for this purpose, such as, for example, condensation, by cooling, of the jet of gas to be converted.

The temperature of entry of the gas jet into the discharge zone is advantageously between 0 and 800°C, preferably between 400 and 700°C, it being possible for the optional preheating of the entering gas to be provided by recirculation of the effluent gases.

The velocity of the gas jet at the entry of the reactor is an important parameter of the process. This parameter is advantageously set between 5 and 30 m/s, preferably between 7 and 20 m/s and still more preferably at a value of the order of 10 m/s.

According to another particularly advantageous aspect of the process according to the invention the gas to be treated is subjected to a highly turbulent regime in the discharge zone 11 of the generator (turbulence zone).

The electrical arcs and/or discharges are essential for the supply of reactive species permitting the conversion of N_2O into NO_x outside the state of thermodynamic equilibrium. One of the advantages provided by the sliding arcs and/or discharges is a reduced wear on the electrodes.

The electrical power involved is



advantageously between 0.01 and 1, preferably between 0.02 and 0.5 and still more preferably this power is of the order of 0.15 ± 0.05 kWh/kg of entering N_2O .

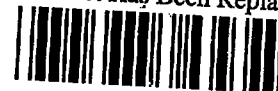
Given that the conversion of N_2O into N_2 and O_2 is highly exothermic (approximately 80 kJ/mol), the thermal decomposition triggered or initiated by the low-temperature plasma generator, operating by forming sliding electrical arcs and/or discharges between the divergent electrodes, is thermally self-supporting.

The examples, which follow, of the process for converting N_2O into NO_x ($x = 1$ or 2) with the aid of the device described above, in accordance with the invention, allow the latter to be better understood and show a few of its advantages and of its alternative forms.

EXAMPLES 1 TO 14:

1. Apparatus:

The device used is similar to that shown in the single figure. The low-temperature plasma generator is capable of producing, on the divergent electrodes, three-phase sliding electrical discharges characterized by high operating voltages (a few kV) and relatively low currents (fractions of amperes). This process is sequential. The lifetime of a discharge is between 5 and 20 milliseconds, depending on the velocity of the gas injected.



2. Reactant-product - reaction

conditions:

Experiments carried out in the present example have been performed by starting with
5 homogeneous mixtures of N_2O with N_2 , O_2 , CO_2 and/or NO , which were stored at a pressure that could attain 67 bars.

The flow rate of the entering gas was varied from 12.7 to 50.5 litres (STP) per minute. The
10 initial temperature of the gas was close to ambient temperature: approximately $25^\circ C$.

In the experiments which follow, the temperature of the entering gas jet varied between 38 and $355^\circ C$.

15 The electrical power dissipated in the reactor was measured with the aid of a three-phase analog energy counter at the input of the supply system. It varied between 0.8 and 2.1 kW.

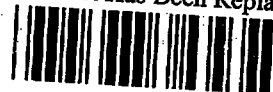
Within the scope of the experiments
20 which follow, the conversion of the NO_x into derivatives such as HNO_3 was not carried out. The gases converted were merely collected for analysis.

3. Analyses:

Two types of analyses were performed: a
25 chromatographic analysis and a chemical analysis.

With regard to the chromatographic analysis, the apparatus and the operating conditions were the following:

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- Chromatograph: Chrompack 9001
- Carrier gas: helium; flow rate 5.5 ml/min
- Two columns: "wide-bore" (GS-Molsieve 30 m x 0.539 mm and GS-Q 30 m x 0.539 mm) and a "back-flush) system
- 5 - Detector: thermal conductivity
- Integrator: Shimadzu C-R5A
- Oven temperature: 30°C
- Calibration: air, N₂O and pure CO₂ before and after a series of experiments
- 10 - Injection: via a 0.25 cm³ gas loop; gas transfer using a 400-cm³ syringe.

Chemical analysis consisted of an acidimetric determination of the NO_x resulting from bringing the output gas mixture into contact with aqueous hydrogen peroxide and determining NHO₃ with NaOH or KOH.

15

4. Results:

Examples 1 to 5 show the effect of the variation in the temperature of the entering gas jet.

20 Examples 6 to 8 are intended to show the effect of the water vapour content in the entering gas jet.

Examples 9 to 12 show what may be the consequences of the variation in the flow rate of the entering gas: 22 to 180 Nl/min.

25

Examples 13 and 14 demonstrate the consequences of the presence of NO₂ in the entering gas.



The parameters and the results of

Example 1 to 14 are given in the table below.

In the latter, "i" and "o" mean "inlet" and "outlet" of the reactor respectively.

5 M = Molecular mass

t = temperature.

DC_{N_2O} = Degree of conversion of N_2O

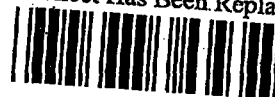
= (number of moles N_2O i- number of moles N_2O o)/number of moles N_2O i

10 Y_{NO} = yield of NO_x

= (number of moles NO_x o- number of moles NO_x i)/(number of moles N_2O i- number of moles N_2O o)

The results are collated in Table 1 below.

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Ex	N ₂ O i mol %	N ₂ i mol %	O ₂ i mol %	H ₂ O i mol %	CO ₂ i mol %	NO ₂ i mol %	Flow rate i Nl/min	T i °C	P elec kW	N ₂ O o mol %	NO ₂ o wt %	DC _{N2O} mol/mol	Y _{NO} mol/mol
1	47.0	41.4	11.6	0.0	0.0	0.0	37.4	38	1.18	28.5	7.5	29.3	42.9
2	47.0	41.4	11.6	0.0	0.0	0.0	45.70	50	1.19	33.1	7.3	19.7	62.2
3	47.0	41.4	11.6	0.0	0.0	0.0	37.4	140	1.16	29.6	8.9	21.9	68.1
4	47.0	41.4	11.6	0.0	0.0	0.0	37.4	226	1.06	27.9	8.8	27.0	54.4
5	47.0	41.4	11.6	0.0	0.0	0.0	37.4	355	1.04	27.7	8.7	28.0	51.7
6	50.9	33.9	10.8	0.0	4.4	0.0	37.4	25	0.97	34.7	8.8	26.1	55.7
7	49.3	32.9	10.4	3.1	4.3	0.0	45.70	25	0.93	33.0	5.1	27.7	30.8
8	47.8	31.9	10.1	6.1	4.1	0.0	37.4	25	0.93	32.7	4.6	27.4	28.4
9	43.8	43.9	12.3	0.0	0.0	0.0	22.00	51	0.88	22.9	8.5	47.2	31.7
10	43.8	43.9	12.3	0.0	0.0	0.0	61	52	0.62	34.1	6.1	23.4	45.9
11	43.8	43.9	12.3	0.0	0.0	0.0	70.40	62	1.09	34.0	5.6	23.2	42.6
12	43.8	43.9	12.3	0.0	0.0	0.0	81.80	53	1.11	30.8	5.0	29.0	30.7
13	31.6	46.2	12.2	0.0	0.0	10.0	46	25	0.98	14.4	17.0	59.2	7.1
14	31.6	45.2	12.7	0.0	0.0	10.6	56	25	1.07	16.8	18.2	51.2	8.5

Table 1





CLAIMS:

1. Process for plasmachemical conversion of N_2O into NO_x ($x = 1$ or 2) and/or into its derivatives, characterized in that the N_2O is brought into contact
5 with at least one electrical arc and/or discharge.

2. Process according to Claim 1, characterized in that it consists:

- in forming a jet of gas to be treated comprising the N_2O ,
- 10 - in directing this jet into the interstitial space (11) of at least two divergent electrodes (10a to 10f) to which electrical voltage is applied, so as to create at least one electrical arc and/or discharge and belonging to a low-temperature plasma generator (4),
15 the latter operating by forming sliding electrical arcs and/or discharges between the electrodes (10a to 10f),
so that the gas travels along the electrodes from the arc and/or discharge zone (11) starting from the arc and/or discharge zone where these electrodes are
20 closest to each other,
- and in recovering the gas comprising the NO_x formed.

3. Process according to Claim 1 or 2, characterized in that the gas containing the NO_x formed
25 is subjected to a conversion treatment making it possible to obtain nitric acid.

4. Process according to Claim 3, characterized in that the treatment is an

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oxydoabsorption with water on a column, preferably in combination with a water quenching.

5 5. Process according to any one of Claims 1 to 4, characterized in that the gas injected into the interstitial space (11) of sliding arcs and/or discharges is free or substantially free from water vapour.

10 6. Process according to any one of Claims 1 to 5, characterized in that the conversion of N_2O into NO_x is carried out at a pressure of between 0 and 10×10^5 Pa, preferably between 0 and 6×10^5 Pa and, still more preferably, at normal atmospheric pressure (10^5 Pa).

15 7. Process according to any one of Claims 1 to 6, characterized in that a temperature of entry into the discharge zone of between 0 and $800^\circ C$, preferably between 400 and $700^\circ C$ is provided for the gas jet.

20 8. Process according to any one of Claims 1 to 7, characterized in that the velocity of the gas jet at the entry of the reactor is set between 5 and 30 m/s, preferably between 7 and 20 m/s and, still more preferably, at a value of the order of 10 m/s.

25 9. Process according to any one of Claims 1 to 8, characterized in that the gas to be treated is subjected to a turbulent regime in the arc and/or discharge zone (11).

10. Process according to any one of Claims 1 to 9, characterized in that the gas to be treated is





free or substantially free from NO_x before moving into the arc and/or discharge zone.

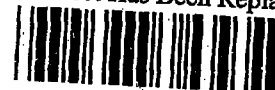
11. Process according to any one of Claims 1 to 10, characterized in that an electrical power dissipated in the reactor is provided which is between 0.01 and 1 kWh/kg of entering N_2O , preferably between 0.02 and 0.5 kWh/kg of entering N_2O and, still more preferably, of the order of 0.15 ± 0.05 kWh/kg of entering N_2O .

12. Device for implementing the process according to any one of Claims 1 to 11, characterized in that it comprises a reactor (1) consisting of an adiabatic enclosure (2) containing a low-temperature plasma generator (4) by forming sliding electrical arcs and/or discharges and means (3) for forming the gas jet.

13. Device according to Claim 12, characterized in that the generator (4) comprises three pairs of diverging electrodes (10a to 10f) connected to means of supply (12) and arranged so that they define a widening arc and/or discharge zone (11).

14. Device according to Claim 13, characterized in that, in addition to the generator (4), it comprises a turbulence zone (11), a zone (6) for conversion of the N_2O into NO_x optionally of "plug" type, and optionally a module for converting the NO_x obtained into nitric acid.

15. Device according to any one of Claims 12



to 14, characterized in that the materials of which the reactor and/or the electrodes consist are ceramics.



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