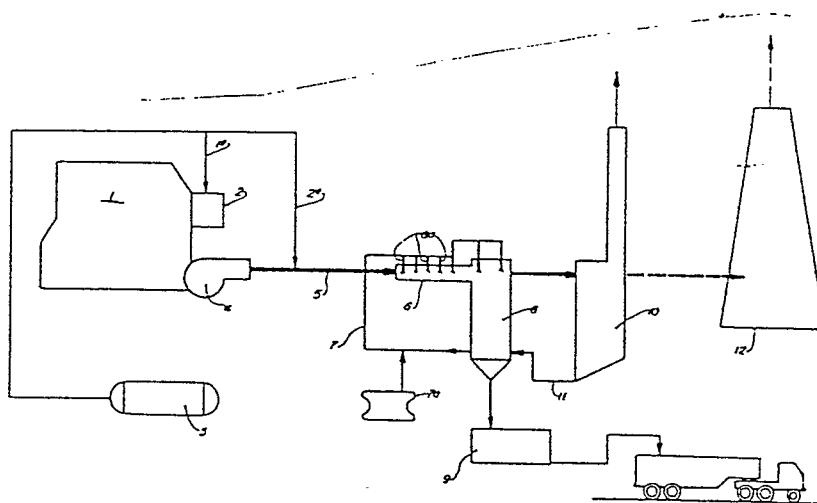




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification³ : B01D 53/34; C01C 1/242</p>	A1	<p>(11) International Publication Number: WO 84/ 00903 (43) International Publication Date: 15 March 1984 (15.03.84)</p>
<p>(21) International Application Number: PCT/BR83/00007 (22) International Filing Date: 25 August 1983 (25.08.83) (31) Priority Application Numbers: PI 8205030 PI 8304413 (32) Priority Dates: 26 August 1982 (26.08.82) 16 August 1983 (16.08.83) (33) Priority Country: BR (71)(72) Applicants and Inventors: LADEIRA, Newton, Gonçalves [BR/BR]; Av. Angélica, 2635 ap. 82, São Paulo, SP (BR). DE OLIVEIRA, Paulo, Roberto, Medeiros [BR/BR]; R. Baronesa de Itú, 698 ap. 32, São Paulo, SP (BR). MARANTE, Adilson, Pinto [BR/BR]; Av. dos Pinheiros nº 4, São Paulo, SP (BR). KREPEL, Pedro, Andrea [BR/BR]; R. Bangú nº 31, São Paulo, SP (BR).</p>	<p>(74) Agent: PEDRAS ARNAUD, Antonio, Mauricio; R. José Bonifácio nº 93, São Paulo, SP 01003 (BR). (81) Designated States: AT (European patent), BE (European patent), DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent), SE (European patent), US. Published With international search report.</p>	

(54) Title: PROCESS TO ELIMINATE AIR POLLUTANTS WHICH RESULT FROM THE COMBUSTION OF FUELS CONTAINING SULPHUR



(57) Abstract

Process to eliminate air pollutants which result from the combustion (1) of fuels containing sulphur, permitting the transformation of substantially all the existing SO₂ and SO₃ produced by the combustion of fuels, to Ammonium Sulphate. In accordance with an accomplishment of this invention, a quantity (1°) of gaseous Ammonia, sufficient to react with all the SO₂ and SO₃, is injected into the combustion gases when these are at a temperature range of 250°C to 600°C, these gases being subsequently cooled down to temperatures below 65°C, and then subjected to separation means to extract the submicron and micra sized particles (6, 7, 8), before being released to the atmosphere. In another accomplishment, a first injection (1°) of Ammonia is made into the 250°C to 600°C combustion gases in a quantity sufficient to fully react with the existing SO₃, and a second Ammonia injection (2°) is made with the combustion gases at a 65°C to 250°C range, and in a quantity sufficient to react with all the existing SO₂ or, if desired, with part of it.

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"PROCESS TO ELIMINATE AIR POLLUTANTS WHICH RESULT FROM THE
COMBUSTION OF FUELS CONTAINING SULPHUR".

TECHNICAL FIELD

The present invention refers to a process aimed at the
5 elimination of air pollution caused by the burning of
Sulphur containing fuels in all kinds of industry and
equipment of all sizes. The process requires less investment
than other alternative processes and produces a commercial
end-product.

10

BACKGROUND ART

One of today's main concerns has been to eliminate air
polluting agents resulting from the burning of Sulphur
containing fuels, without generating inadequate by-products.
Many of the processes presently used require large
15 investments in equipments and installations, normally
without return or with high added operational costs.

DISCLOSURE OF INVENTION

Aiming at solving or minimizing these problems, this process
has been developed. Basically simple, easily retrofitted
20 into the polluting equipments, with low investment costs,
this process produces a high value end-product.

Specifically, the aim of this invention is to transform all
Sulphur Dioxide (SO_2) and Sulphur Trioxide (SO_3) existing in
the combustion gases, to Ammonium Sulphate. This is obtained
25 through the reaction of SO_3 and SO_2 with Ammonia, preferably
in gaseous state, which is injected directly into the
combustion gases. The collected stable end-product is
Ammonium Sulphate $[(NH_4)_2 SO_4]$ which is separated from the
flue gases.

30 These and other objectives of this invention are obtained by

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this process which comprises the following steps: undertake at least one injection of Ammonia (NH_3) in the combustion gases at temperatures between 250°C and 600°C , in quantity sufficient to react with all the SO_3 which is present and with part of the existing SO_2 ; cool the gases to a temperature lower than about 65°C ; separate the submicron and micron size particles from the combustion gases; collect the $(\text{NH}_4)_2 \text{SO}_4$ from the separating equipment, and send the desulphurized combustion gases to the flue.

Considering the possibility of providing more than one injection point of Ammonia (NH_3), this process has foreseen the division of the injection into: a first injection of gaseous NH_3 (Ammonia) into the 250°C to 600°C combustion gases and in a quantity sufficient to react with all the present SO_3 , and a second injection of gaseous NH_3 at a region where the combustion gases are at a 65°C to 250°C temperature range and in a quantity sufficient to react with at least a part of the existing SO_2 .

In this case, the first injection is directed mainly the neutralization of the SO_3 .

In case of injection of all the Ammonia (NH_3) in the 250°C to 600°C combustion gases temperature range, the NH_3 will react with all present SO_3 and the rest of NH_3 will intermix with the combustion gases stream, up to the point where the temperature permits the occurrence of an irreversible reaction between the SO_2 and NH_3 .

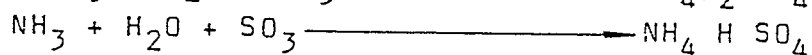
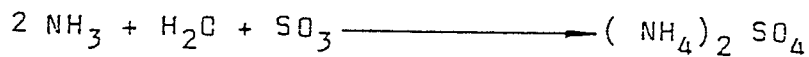
As already established technically, the SO_3 is a gas formed during the combustion of Sulphur containing fuels, by the reaction of gaseous SO_2 with molecular Oxygen (O_2), by the reaction of SO_2 in the flame with atomic Oxygen and by catalytic oxidation of SO_2 in the heat transfer surfaces under high temperatures. The corresponding reactions are

the following:

$$\begin{array}{l} \text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \\ 2 \text{SO}_2 + \text{O}_2 \longrightarrow 2 \text{SO}_3 \\ \text{S} + 3 (\text{O}) \longrightarrow \text{SO}_3 \end{array}$$

Without the presence of catalysers, the burning of Sulphur containing fuels results in up to 5% SO_3 in the total of SO_x compounds. In spite of the fact that gaseous Ammonia reacts with SO_3 in the temperature range of 250°C to about 600°C ,
 5 it has been verified that the ideal temperature range is 300°C to 400°C . In this range, the reaction of SO_3 with NH_3 is instantaneous resulting in $(\text{NH}_4)_2 \text{SO}_4$ (Ammonia Sulphate) and eliminating the possibility of corrosion in the surfaces which would have been contacted by the SO_3 . This corrosion
 10 occurs due to the formation of liquid Sulphuric Acid (H_2SO_4) when SO_3 and water of combustion (H_2O) combine at temperatures below the Sulphuric Acid dew point. The quantity of injected NH_3 is sufficient to insure the formation of $(\text{NH}_4)_2 \text{SO}_4$ (Ammonium Sulphate).

15 Smaller quantities of NH_3 would result in the formation of Hydrogen Ammonium Sulphate ($\text{NH}_4 \text{H SO}_4$), which is a corrosive compound. The corresponding reactions are the following:

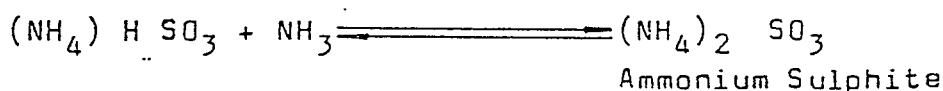
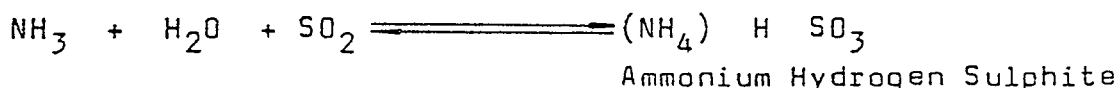


20 The minimum calculated quantity of NH_3 to avoid formation of $\text{NH}_4 \text{H SO}_4$ in 3% Sulphur bearing fuel oils, for example, is 0,08% of the oil weight. For higher levels of Sulphur, the percentage will correspondingly higher (up to 9%). The reaction product $(\text{NH}_4)_2 \text{SO}_4$ is stable and is carried
 25 together with the combustion gases' stream. As previously mentioned, this process is directed towards a complete and reliable elimination of the SO_2 resulting from the combustion of liquid, solid or gaseous fuels.

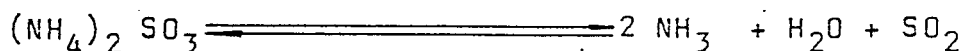
To neutralize the SO_2 , the gaseous NH_3 is injected in one or
 30 more locations of the equipment, where the combustion gases are at a range of 65°C to 600°C . If the gaseous NH_3 is totally injected in a 200°C to 600°C region, the excess portion which does not participate in the reaction with SO_3 , is carried in the combustion gases' stream, forming an
 35 intimate mixture which will react when the right temperature

range is reached.

At 120°C the quantities of SO₂ which react with NH₃ increases, and as the temperature of the gases decreases to about 108°C, an equilibrium situation is reached with 35% to 5 40% of the existing SO₂ having reacted with NH₃ according to the following reversible reactions:

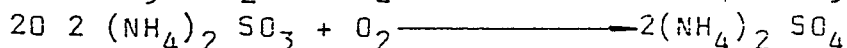
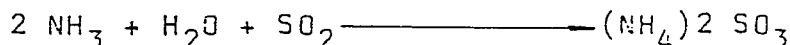


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It has been experimentally verified that this equilibrium situation is maintained until temperatures in the range of 65°C are attained.

15 Between 65°C and 48°C it has been experimentally proven that this reaction is stable with the simultaneous oxidation of Ammonium Sulphite to Ammonium Sulphate according to the following reactions:



This oxidation is processed by existing combustion air in excess or by an extra air entrainment into the gases, just before the separation system. The (NH₄)₂ SO₄ (Ammonium Sulphate) is a stable, solid, submicron to a low value micra 25 sized, product.

The above mentioned facts lead to verified results, if the combustion gases are released at higher temperatures than 65°C, part of the SO₂ (even if already reacted) might be released to the atmosphere, due to the reversible nature of 30 the reactions at that higher range.

The separation of the stable end-product (NH₄)₂ SO₄ (Ammonium Sulphate) from the combustion gases' stream, can be accomplished by dry methods such as Electrostatic Precipitators or other kinds of filters, or more economically 35 by wet processes such as water absorbers.

5

The absorption of $(\text{NH}_4)_2 \text{SO}_4$ (Ammonium Sulphate) in water is possible due to the highly soluble nature of this product.

DESCRIPTION OF THE DRAWINGS

The process will now be briefly outlined so as to show an
5 example of a feasible and tested lay-out of the Desulphurization of Combustion Gases with Ammonia.

Figure n° 1 represents a flow diagram of the main components
of an installation comprising the equipment where the Sulphur
bearing fuel is burned, two distinct Ammonia injection
10 points, the $(\text{NH}_4)_2 \text{SO}_4$ wet absorption system, an entrained
water separator, the dessulphurized flue gases released to
atmosphere and the concentrated Ammonium Sulphate solution
collection system.

Figure n° 2 illustrates one of the several assemblies of the
15 Ammonia injection elements, in adequate locations of the
combustion gases' stream.

Figure n° 3 shows a typical configuration of the NH_3
injection tubes.

BEST MODE OF CARRYING OUT THE INVENTION

20 As shown in Figure 1, this process is applied in industrial
installations such as boilers, furnaces, ovens, dryers, etc
(1), burning Sulphur bearing fuels. Heat recovery equipment
(2) may or not be present. In the present process, NH_3
coming from a storage tank (3) is distributed in gaseous or
25 liquid form. If as a liquid, NH_3 is vaporised or not and
injected initially in a region where the gases are preferably
between 250°C and 600°C and before the heat recovery
equipment. The quantity of the first injection is, as
previously explained, adequate to insure complete reaction
30 with the SO_3 , therefore eliminating corrosion problems in
the heat recovery or other metallic or non metallic
components of the existing installation. This permits the
use of cheaper construction materials or results in longer
life of the existing ones.

35 The combustion gases which leave the heat recovery equipment



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(2) in the example shown, are conducted by means of a duct (5) and ventilator (4) to a point where a second injection of gaseous NH_3 is undertaken at lower temperature levels. Even if the gaseous NH_3 is injected at only one location, 5 the quantity will always be such as to react initially with the existing SO_3 and further on at lower temperatures with the SO_2 .

The combustion gases, after the last NH_3 injection, are sent along the duct (5) and into an appropriately dimensioned duct 10 (6). This duct (6) has a battery of atomizing nozzles (6a) in adequate number and sizing.

These nozzles spray a recirculating solution of Ammonium Sulphate into the combustion gases. This solution is recirculated under pressure by a pump and piping (7).

15 A water make-up system (7a) is hooked up into this recirculating system. This pre-washing phase insures initial absorption of the existing $(\text{NH}_4)_2 \text{SO}_4$ particles and a severe temperature drop of the combustion gases. Depending on the inlet temperature of the gases to this pre-washer/absorber, 20 the completion of the SO_2 reaction to $(\text{NH}_4)_2 \text{SO}_4$, may also happen in this region.

In the second stage of the $(\text{NH}_4)_2 \text{SO}_4$ (Ammonium Sulphate) absorption in water, the combustion gases pass through a high pressure injector (8a) (or additional nozzles) spraying 25 $(\text{NH}_4)_2 \text{SO}_4$ solution into the gaseous stream, which is assembled on top of a solution collection tank (8). At this phase the simultaneous retention of the soluble Ammonium Sulphate particles and of the insoluble particles such as carbon, inorganic materials, etc, is achieved.

30 The concentrated solution of Ammonium Sulphate may be continuously or periodically taken away from the collection tank (8) into a storage tank (9).

This volume is substituted by make-up water.

One of the advantages of this wet separation process is that 35 the insoluble and undesirable particles can be easily

separated from the dissolved Ammonium Sulphate solution by conventional filters or gravity settling.

The system has also foreseen, for the cases where water entrained as mist should not be lost, the installation of a
5 low pressure drop demister (10) which recovers part of the water which is returned to the solution tank (8) by piping (11).

The combustion gases leave the solution tank (8) totally desulphurized or, if desired, within the SO_2 emission levels
10 specified by the local Environmental Control Agency. The emission level is easily adjusted by the variation of the Ammonia flow to be injected, with the use of proportioning or manual valves and flowmeters.

The complete system can also receive a pH controller of the
15 tank (8) solution to insure continuous neutralization of the SO_2 .

Direct or indirect measurement systems of the Ammonium Sulphate concentration in the solution contained in the tank (8) can also be added.

20 The duct (5) which receives the combustion gases, can also remain connected to the existing chimney (12) through a normally closed gate valve which functions as a by-pass to the separation system.

As shown in figures 2 and 3, the Ammonia gas injection is
25 made in the gas ducts through perforated tubes (20), the number and disposition of the tubes being determined by the calculated Ammonia gas flow, and by the objective of obtaining complete intermixing with the combustion gases. The tubes are preferentially built out of mild steel and
30 completely cross the combustion gas ducts, each tube being divided in three equal parts, with different number and sizes of holes (21), as better detailed in figure 3. The first part has two series of holes (21) with a diameter d and a spacing of x . The second part has two lines of d_1
35 diameter holes, where d_1 is larger than d and spaced in an

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interval x_1 , smaller than x . Likewise the third part has d_2 diameter holes (d_2 larger than d_1) spaced at x_2 intervals smaller than x_1 .

The usual installation requires two parallel tubes (fig.2).

5 In this case, the NH_3 gas will enter one tube from the right end of the duct while the other tube enters from the left. The NH_3 gas always enters the tube going through the d diameter, x spaced holes (21).

A plug (30) blocks the end of each tube. The two series of 10 holes of each tube (fig. 3) are located so that a hole of one series is always in between two holes of the other series.

CLAIMS

1. A process to eliminate air pollutants resulting from the combustion of sulphur bearing fuels, characterized in that it comprises the following steps:
- 5 . provide at least one injection of Ammonia into 250°C to 600°C combustion gases, in sufficient quantity to transform substantially all the existing SO₃ and SO₂ (produced by the combustion of these fuels) into Ammonium Sulphate;
 - . cool the combustion gases to a temperature lower than 65°C;
 - 10 . pass these gases through a separation system adequate for submicron to low value micra particulates;
 - . collect the Ammonium Sulphate end-product from the separation system;
 - . release the desulphurized gases to the atmosphere.
- 15 2. A process as claimed in claim 1, characterized in that the Ammonia injection is made with the combustion gases being at a temperature range of about 250°C to 400°C.
- . 3. A process as claimed in claim 1, characterized in that the injection phase comprises:
- 20 . a first injection of Ammonia into the combustion gases when these are at a 250°C to 600°C temperature range and in sufficient quantity to react with all the SO₃ formed during by the combustion of these fuels;
 - . a second injection of Ammonia into the combustion gases
 - 25 when these are at a 65°C to 250°C temperature range, and in a sufficient quantity to react with substantially all SO₂ or, if desired, with part of the SO₂, so as to be within the local limits for emission of SO₂, as established by the Environmental Authorities.
- 30 4. A process as claimed in claim 3, characterized in that



10

the first injection of Ammonia is made with the combustion gases when they are at a temperature range of 300°C to 400°C and second injection of Ammonia with the gases at 65°C to 120°C range.

- 5 5. A process as claimed in any one of the claims 1 or 2, characterized in that the separation means include absorbers with water, with the resulting Ammonium Sulphate Solution being separated from the desulphurized combustion gases.
6. A process as claimed in claim 5, characterized in that
10 the cooling of the combustion gases to temperatures under 65°C can also be completed in the separation system.
7. A process as claimed in any one of the claims 1 to 4, characterized by the fact that the Ammonia is preferably injected in gaseous state.
- 15 8. A process as claimed in claim 7, characterized in that the injection of Ammonia, when as gas, is made by means of perforated tubes installed transversally to the combustion gases' stream.

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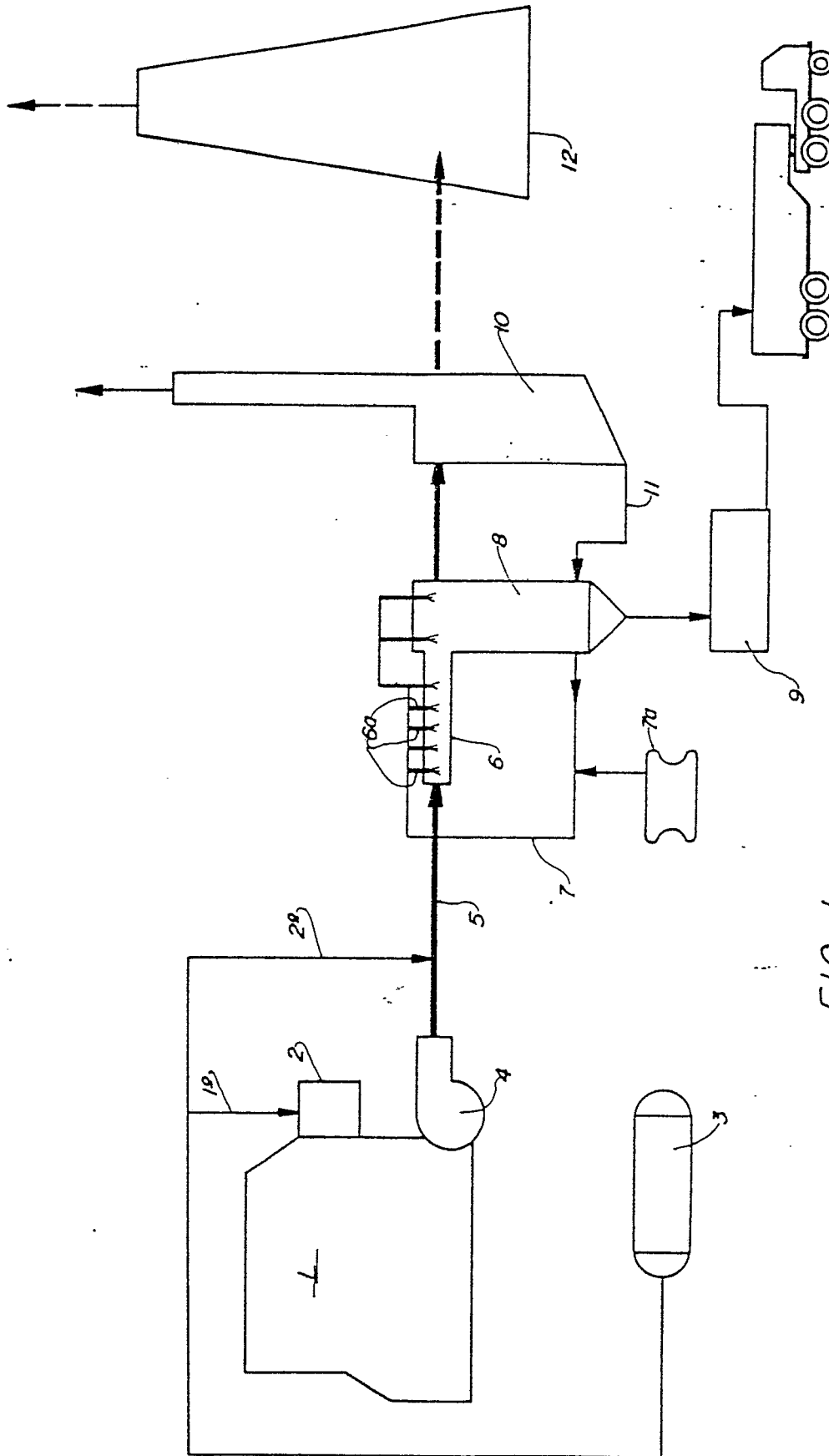


FIG. 1



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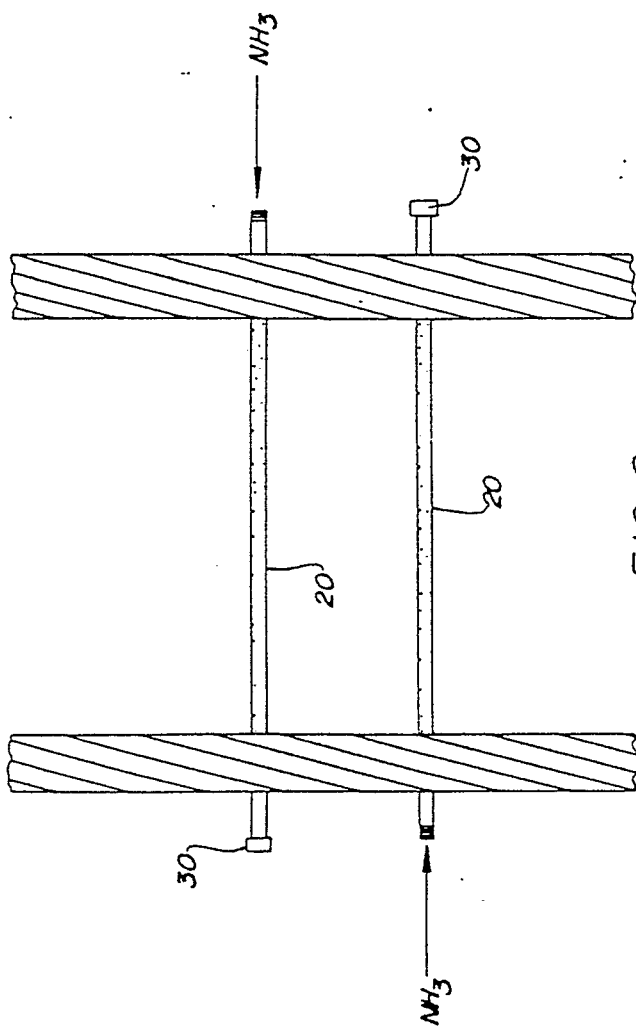


FIG. 2

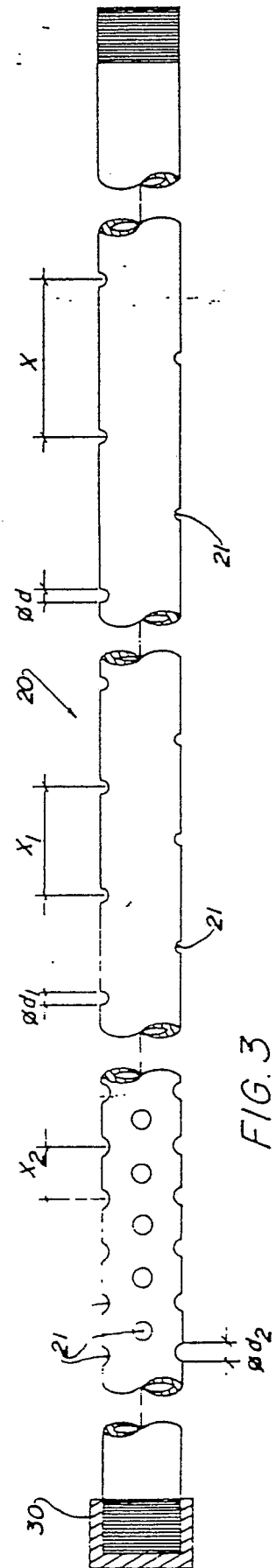
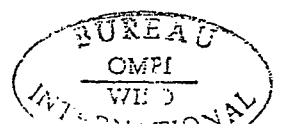
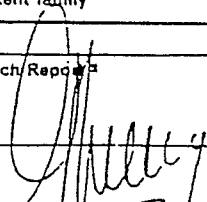


FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No. **PCT/BR 83/00007**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ³ : B 01 D 53/34; C 01 C 1/242		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC ³	B 01 D 53/08; C 01 C 1/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁴
A	Chemical Abstracts, vol. 95, no. 12, September 1981 (Columbus, Ohio, US) see page 279, abstract no. 102276y, U. Mohn: "Process for removing sulfur oxides from gases with direct production of a usable finished reaction product", Report 1979, BMFT-FB-T-79-90 (Ger)	1,7
A	FR, A, 1388690 (OFFICE NATIONAL INDUSTRIEL DE L'AZOTE) February 1965	
A	FR, A, 2364682 (I.F.P.) 14 April 1978	
A	FR, A, 2382263 (Dr. C. OTTO & COMP.) 29 September 1978	
A	US, A, 4064219 (YUZO YAMASHITA) 20 December 1977	
A	GB, A, 1104583 (G. PETERSEN) 28 February 1968	./.
<p>⁶ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ³	Date of Mailing of this International Search Report ³	
24th November 1983	13 DEC. 1983	
International Searching Authority ¹	Signature of Authorized Officer ¹⁰	
EUROPEAN PATENT OFFICE	 G.L.M. Kruidenberg	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category*	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US, A, 3928536 (G.W. LEWIS) 23 December 1975	
A	GB, A, 2004259 (Dr. C. OTTO) 28 March 1979	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/BR 83/00007 (SA 5644)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/12/83

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 1388690		None	
FR-A- 2364682	14/04/78	NL-A- 7710275 BE-A- 858705 DE-A- 2741972 GB-A- 1543494 JP-A- 53039265 US-A- 4180550 CA-A- 1103898 SE-A- 7710463 SE-B- 418391	22/03/78 15/03/78 23/03/78 04/04/79 11/04/78 25/12/79 30/06/81 21/03/78 25/05/81
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US-A- 4064219	20/12/77	None	
GB-A- 1104583		NL-A- 6516530 DE-A- 1544094 US-A- 3510253 BE-A- 672857 DE-A- 1544099	20/06/66 10/07/69 05/05/70 16/03/66 27/11/69
US-A- 3928536	23/12/75	US-A- 4003986	18/01/77
GB-A- 2004259	28/03/79	BE-A- 870397 LU-A- 80215 NL-A- 7808767 FR-A- 2402469 DE-A- 2741116 JP-A- 54050473 US-A- 4268489 CA-A- 1107036	02/01/79 07/03/79 15/03/79 06/04/79 22/03/79 20/04/79 19/05/81 18/08/81

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82

INTERNATIONAL APPLICATION NO.

PCT/BR 83/00007 (SA 5644)

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82