

Process and filter for preparing NO₂-free nitrogen monoxide using sulfur-containing polymers

The invention relates to a process for preparing nitrogen-dioxide-free gases and liquids and a filter for
5 the selective removal of nitrogen dioxide from gases and liquids.

Nitrogen monoxide gas or nitrogen monoxide gas mixtures which are free of nitrogen dioxide are required in exhaust gas metrology for the calibration of measurement
10 and analysis systems.

Recently, the medical use of nitrogen monoxide (NO) has attained particular importance. In patients having serious pulmonary symptoms, addition of NO to the breathing air can decrease the blood hypertension in the
15 pulmonary circulation. In combination with the broncho-dilatory action of NO, an improved aeration of diverse lung sections and thus also improved gas exchange occurs.

The colorless nitrogen monoxide (NO) rapidly reacts with molecular oxygen to form brown nitrogen dioxide (NO₂). In
20 the presence of air or on the admission of air, NO₂ is therefore formed from NO. NO₂ - owing to the ubiquitous oxygen - is therefore an inherent impurity of NO. Especially in the event of a medical use of NO, owing to its toxicity, the content of NO₂ must be very low. There
25 has therefore been no lack of attempts to selectively absorb or convert to NO the NO₂ once formed.

The catalytic conversion of NO₂ to NO in the presence of oxygen according to:



- at a Cu, Mo or Ni catalyst at temperatures of $> 220^{\circ}\text{C}$ is possible. This method is employed in the separate determination of NO and NO_2 by the chemoluminescence method. (see operation and maintenance instructions for the NO_x measurement instrument CSI 1600 from Columbia Scientific Industries, Austin, Texas, 1980). Disadvantages in this process are the high temperature required and the possibility of recombination of $\text{NO} + \text{O}_2$ to give NO_2 after the gas stream has cooled.
- 10 It is further known that NO_2 dissolves very readily in concentrated inorganic acids such as HNO_3 or H_2SO_4 . NO can therefore be very readily purified by the abovementioned acids using a gas scrubber (A. Golloch, Anorganisch-chemische Präparate [Inorganic Chemical Preparations], 15 Walter de Gruyter Verlag 1985, pp. 232 ff.). A disadvantage in this case is the relatively high expenditure in terms of safety and chemical engineering.

- Further methods are the fractional condensation and distillation to remove NO_2 from NO. A summarizing presentation of the purification processes for NO is found in: 20 G. Brauer, Handbuch der präparativen anorganischen Chemie [Handbook of preparative inorganic chemistry], volume 1, pp. 470 ff., 3rd edition (1975), Verlag F. Enke.

- The object is to find a simple process and a filter for 25 the selective removal of NO_2 from NO_x -containing gases or liquids.

- It has been shown that a selective removal of NO_2 from NO or NO-containing media such as gases or liquids can be carried out highly efficiently by contacting them with a 30 sulfur-containing polymer, preferably poly(arylene thioether), in particular poly(phenylene sulfide).

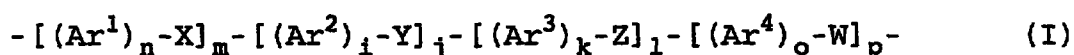
The invention therefore relates to a process for preparing NO-containing gases or liquids which are free of NO_2 , which comprises contacting an NO_x -containing gas or

an NO_x-containing liquid with a material which contains a sulfur-containing polymer; NO₂ is preferably removed from an NO-containing gas mixture.

5 The expression "free of NO₂" means that the content of NO₂ in a medium is less than 1 ppm.

NO_x is used as a collective term for nitrogen oxides NO, NO₂ and N₂O and also includes mixtures of these oxides.

10 Sulfur-containing polymers are, for example, linear or branched polyaryl systems (mean molecular weight, Mw: 4000-200,000) having the repeating unit of the formula I which contain at least one thioether group,

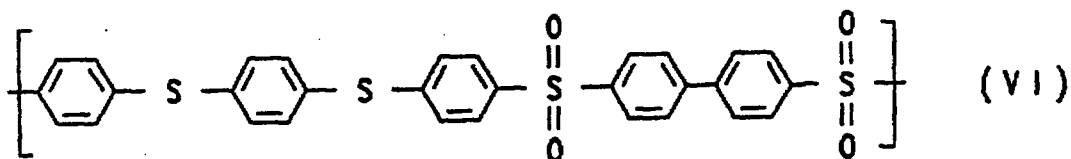
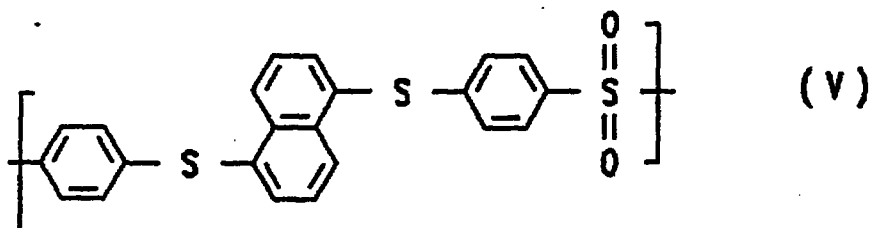
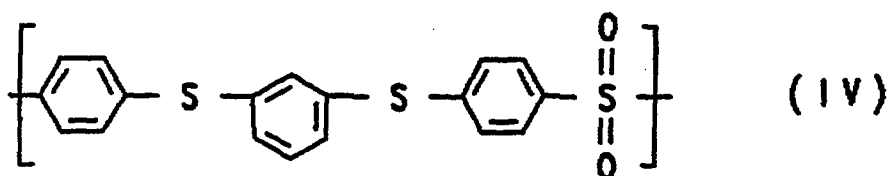
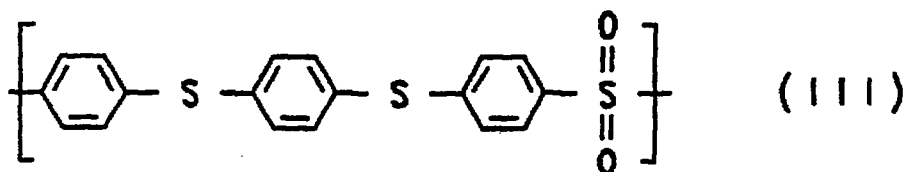
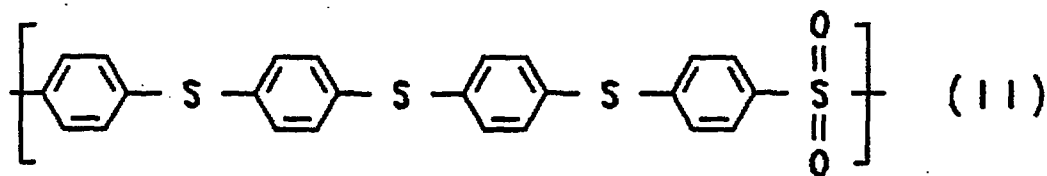


15 where Ar¹, Ar², Ar³, Ar⁴, W, X, Y and Z, independently of each other, are identical or different. The indices n, m, i, j, k, l, o and p are integers from 0 to 4, where their sum must be at least 2. Ar¹, Ar², Ar³ and Ar⁴ are in the formula (I) simple or directly para-, meta- or ortho-linked aryl systems having 6 to 18 carbon atoms. W, X, Y and Z are linking groups, selected from the group consisting of -SO₂-, -S-, -SO-, -O-, -CO-, -CO₂-, alkyl and
20 alkylidene groups having 1-6 carbon atoms and -NR¹- groups, where R¹ is alkyl or alkylidene groups having 1-6 carbon atoms. The aryl systems of the formula (I), in the context of the invention, depending on their chemical
25 structure can further additionally contain, independently of each other, one or more usual functional groups, e.g. alkyl radicals, halogens, sulfonic acid, amino, nitro, cyano, hydroxyl or carboxyl groups. In addition, block copolymers of units of the formula (I) may also be used.

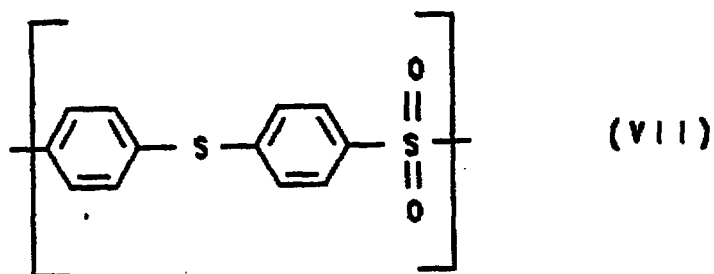
30 The interaction of the sulfur-containing polymers such as poly(arylene thioether) with NO is negligibly small in comparison to the interaction with NO₂, therefore separation of NO₂ from an NO_x-containing gas stream is poss-

ible.

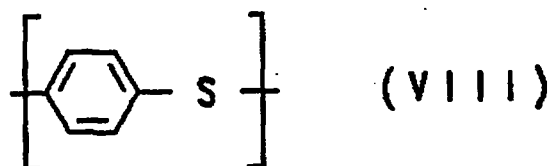
Preferred sulfur-containing polymers are polyarylenes having repeating units of the formulae (II-VI) whose syntheses are described, e.g., in Chimia 28(9), 567:



- 5 and poly(arylene thioethers) having repeating units of the formula (VII) which are described, e.g., in US-A-4,016,145.



Particularly preferred sulfur-containing polymers are poly(phenylene sulfides) (PPS) having the repeating unit of the formula (VIII), whose preparation process is described, e.g., in the patent documents US 3,919,177, US 4,038,262 and US 4,282,347.



PPS of the formula (VIII) can also have, up to a content of 50 mol percent, a 1,2- and/or a 1,3-linkage at the aromatic nucleus. PPS is taken to mean both the linear and also the crosslinked material. In addition, the PPS of the formula (VIII) can contain, per aryl unit, independently of each other, 1 to 4 functional groups, e.g. alkyl radicals, halogens, sulfonic acid, hydroxyl, amino, nitro, cyano or carboxyl groups.

If poly(arylene thioethers) according to the invention are used, in general poly(arylene thioethers) are suitable which have a mean molecular weight of 4000 to 200,000, preferably 10,000 to 150,000, in particular 25,000 to 100,000 (determined by gel permeation chromatography).

The sulfur-containing polymers can be used as powder, fiber, nonwoven web, woven fabric, film, sintered material, molding or as a coating or impregnation of support materials. Moldings having a particularly large surface area may be produced by suitable processes, e.g.

- having a grating or honeycomb structure. The powders have, e.g., commercial particle sizes, granules also being usable. It is important in this case that the gas to be treated or the liquid can be passed without obstruction through the polymer material, for example in the form of a powder fixed bed. If the polymers are used as fibers, these are used as staple fibers, needle-felt, "nonwoven" material, carded sliver or woven fabric. Films or film shreds can also be used in suitable form.
- 10 Coatings of support materials with sulfur-containing polymer such as poly(phenylene sulfide) can be obtained by applying solutions of the sulfur-containing polymer to the support material. Impregnations are made e.g. by impregnating an absorbent support material. Support
- 15 materials which are used are generally inorganic substances such as glass, silica gel, alumina, sand, ceramic compositions, metal and organic substances such as plastics.
- E.g. metals, in particular noble metals and transition
- 20 metals, or metal oxides such as transition metal oxides, can also be applied to the sulfur-containing polymers, for example by superimpregnation, which metals or metal oxides are then present e.g. in the form of small clusters.
- 25 The process according to the invention can be carried out at any temperature which lies beneath the softening point of the polymers used. The application temperatures generally lie in the range from minus 30 to +240°C, preferably minus 25 to +220°C.
- 30 Nitrogen dioxide is generally removed quantitatively, the reaction times depending on the flow velocity, the surface of the purification material, the geometry of the absorber and the temperature. Generally, the time of contact of the sulfur-containing polymer with the medium
- 35 to be purified is in the range from 0.001 seconds to 10

minutes, preferably 0.01 seconds to 5 minutes. However, the times can also be exceeded.

In the removal of NO_2 from NO -containing gas or NO_x -containing liquid, no volatile products are formed
5 from the polymer.

The sulfur-containing polymer, e.g. poly(arylene thio-ether), can generally be used as unblended material. However, addition of conventional fillers such as chalk, talc, clay, mica, and/or fibrous reinforcements, such as
10 glass fibers and/or carbon fibers, whiskers and other conventional additives and processing aids, e.g. lubricants, release agents, antioxidants and UV stabilizers is also possible.

The process according to the invention can be employed
15 with NO_x -containing gas streams and liquids. The process operates e.g. with gases having an NO content in the range from 60% by volume to 1 ppb, preferably 50% by volume to 10 ppb and in particular 40% by volume to 50 ppb. The NO_2 content which can be separated off is in
20 the range from 50% by volume to 1 ppb, preferably 20% by volume to 10 ppb and in particular from 10% by volume to 10 ppb. The ratio between NO and NO_2 in the gases or liquids to be treated can in this case be from 1,000,000:1 to 1:1,000,000, preferably from 10,000:1 to
25 1:10,000 and in particular from 1000:1 to 1:1000.

In the process according to the invention, the removal of NO_2 can be effected e.g. by using a filter which contains a sulfur-containing polymer. The removal of NO_2 from liquids or gases can also be performed for example by
30 swirling up a powder which contains sulfur-containing polymer. This can be effected by stirring a powder in a liquid. The process for removing NO_2 from liquids or gases, as is the case with other conventional adsorption processes for purifying gases or liquids or as is the
35 case with separation processes which are based on an

adsorption process, can be carried out in a batch or column process.

The invention further relates to a filter for removing NO_2 from NO_x -containing gases or NO_x -containing liquids,
5 which filter contains a sulfur-containing polymer.

The specifications for the sulfur-containing polymer which were given in connection with the process according to the invention correspondingly apply to the filter.

The filter can also be operated in combination with other
10 filter materials, e.g. dust filters.

The filter which contains a sulfur-containing polymer can contain the filter material e.g. in the form of a powder packed bed, a nonwoven web, a nonwoven web/powder mixture, a grating structure or honeycomb structure.
15 However, the powder can also be incorporated into non-woven webs of other materials.

The process and the filter are particularly suitable for producing NO test gases, in which case e.g. an NO crude gas which is contaminated by NO_2 and contains a high NO
20 concentration is passed through the filter and is purified in the course of this and is then diluted to the desired concentration using an oxygen-free gas. The dilution and filtration steps can also be carried out in parallel or in reverse order.

25 The process and the filter according to the invention can further be used in medical technology. Thus, for example, in a treatment using NO uptake via the lung, the NO-containing gas and the added air can be combined upstream of or in the filter and thus breathing in of an
30 NO_2 -free gas mixture can be achieved. The filter can comprise for example a breathing mask in the intake stream of which is inserted the filter containing the sulfur-containing polymer.

The filter according to the invention can be used to generate NO₂-free nitrogen monoxide/nitrogen/air mixtures for treating IRDS (IRDS = Infant Respiratory Distress Syndrome), ARDS (= Acute Respiratory Distress Syndrome, also = Adult Respiratory Distress Syndrome), lung failure, migraines, persistent pulmonary hypertonia based on left myocardial insufficiency or for improving lung function.

Examples:

- 10 1.) A so-called NO crude gas comprising approximately 20% by volume NO in nitrogen which was contaminated with 795 ppm of NO₂ due to its preparation was passed through a filter cartridge which was packed with poly(phenylene sulfide) (Mw: 30,000, melting point T_m: 288°C) in the
15 form of granules (mean particle diameter approximately 1 mm). The absorption section is characterized by the following parameters:

	Internal diameter:	2.5cm
	Bed height:	32.5 cm
20	Mass:	100.5 g
	Throughput:	100 l/h

At the exit of the absorber bed the gas was analyzed using an FTIR spectrophotometer (manufacturer: Perkin-Elmer, Überlingen, Federal Republic of Germany) and an
25 NO/NO₂ chemoluminescence measuring instrument (Type CSI 1600, Columbia Scientific Instruments, Austin, Texas, USA) for NO₂ and NO contents. In the entire period of 4 hours over which measurements were taken, the NO₂ concentration was beneath the detection limit of 100 ppb.

- 30 2.) A gas mixture of 158 ppm of NO₂ in nitrogen was passed through a filter cartridge as in Example 1. Immediately at the exit of the filter, the NO₂ content of the gas mixture was determined by IR spectroscopy. The NO₂ concentration was beneath the detection limit.

3.) In a similar manner to Example 1, the capacity of the filter mentioned in Example 1 was determined using a gas mixture of 1% by volume NO_2 and 99% by volume nitrogen. The gas mixture was passed through the filter until the
5 NO_2 content of the gas downstream of the filter increased above an NO_2 content of 1 ppm. The amount of gas which flowed through the filter until the set limit of NO_2 content was achieved was defined as the absorption capacity of the filter. At a temperature of 22°C , an
10 absorption capacity resulted of approximately 2% by weight of the filter mass.

Patent claims

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1. A process for preparing NO-containing gases or liquids which are free of NO₂, which comprises contacting an NO_x-containing gas or an NO_x-containing liquid with a material which contains a sulfur-containing polymer.
2. A filter for removing NO₂ from NO_x-containing gases or NO_x-containing liquids, wherein it contains a sulfur-containing polymer.
3. The process as claimed in claim 1 or filter as claimed in claim 2, wherein the sulfur-containing polymer is a poly(arylene thioether).
4. The process as claimed in claim 1 or 3 or filter as claimed in claim 2 or 3, wherein the sulfur-containing polymer is a poly(phenylene sulfide).
5. The process as claimed in one or more of claims 1, 3 or 4, wherein NO₂-free NO gas or NO₂-free NO gas mixtures are generated.
6. The process as claimed in one or more of claims 1, 3, 4 or 5 or filter as claimed in any of claims 2 to 4, wherein the sulfur-containing polymer is used as powder, fiber, nonwoven web, woven fabric, film, film parts, sintered material, molding, combination of two or more of the said embodiments or as a coating or impregnation of support materials.
7. The process as claimed in one or more of claims 1 and 3 to 6 or filter as claimed in any of claims 2 to 4 or 6, wherein the sulfur-containing polymer has a mean molecular weight in the range from 4000 to 200,000 atomic weight units.
8. The process as claimed in one or more of claims 1

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and 3 to 7, wherein the removal of the nitrogen dioxide is performed at temperatures of minus 30 to +240°C, preferably minus 25 to +220°C.

- 5 9. The use of a filter as claimed in claim 2 as a respiratory protection filter.
10. The use of a filter as claimed in claim 2 for generating NO₂-free NO gas or NO₂-free NO gas mixtures, in particular for generating NO₂-free test gases.
- 10 11. The use of a filter as claimed in claim 2 for generating NO₂-free nitrogen monoxide/nitrogen/air mixtures for medical applications.
- 15 12. The use of a filter as claimed in claim 2 for generating NO₂-free nitrogen monoxide/nitrogen/air mixtures for treating IRDS, ARDS, lung failure, migraines, asthma, persistent pulmonary hypertonia based on left myocardial insufficiency or for improving lung function.



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