

Method for the recovery and/or separation of sulphur
oxyfluorides from gas mixtures

Description

The invention relates to a method for the recovery or separation of sulphur oxyfluorides from gas mixtures, in particular for the recovery of sulphuryl fluoride (SO_2F_2) or thionyl fluoride (SOF_2) from air or exhaust air which is contaminated therewith.

DE 197 08 669 describes a method for the fumigation of spaces by introducing a fumigation agent and continuously withdrawing the treatment atmosphere, wherein the fumigation agent can be separated e.g. in an adsorber and can be re-used after desorption. Coal particles or aluminium oxide particles are mentioned as adsorption agents, and inter alia sulphuryl fluoride as fumigation agent. Sulphuryl fluoride can be and is used as a pesticide. For example pests in fresh wood or wood used in buildings (woodworm, fungi), in storage spaces or in mills (granary weevils) or textiles can be controlled using SO_2F_2 . In this case, SO_2F_2 is used on its own or in combination with other known pesticides. Once fumigation has ended, usually the SO_2F_2 is decomposed by heat or destroyed by lye. The secondary products produced thereby can frequently be disposed of only on special waste dumps.

It is desirable to work up gas mixtures of this type with the aim of being able to re-use the sulphur oxyfluorides.

The object of the present invention is to provide a method for the separation of gas mixtures, in which virtually no environmentally damaging constituents of the gas mixtures pass into the atmosphere and the components which are

separated off can be re-used. Furthermore, no secondary products which have to be disposed of should be produced.

According to the invention, gas mixtures containing sulphur oxyfluoride are contacted with adsorbents and/or membranes for recovery of the sulphur oxyfluorides and the sulphur oxyfluorides which are separated off are sent for re-use, optionally after desorption, depending on requirements. The air which is low in or freed of sulphur oxyfluoride from the gas mixture can be let off into the atmosphere without hesitation.

In particular SO_2F_2 , SOF_4 , SOF_2 are to be understood as sulphur oxyfluorides within the spirit of the invention. Gas mixtures having a sulphur oxyfluoride content from 5 ppmv or 20 mg/m³ onwards may be separated.

According to the invention, the gas mixture is passed through at least one adsorption stage and/or membrane stage containing or consisting of zeolites, which have an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the so-called modulus, >10 preferably >100, a particle size >1 mm, preferably >2 mm, and a pore diameter of 0.4 to 0.7 nm, preferably 0.5 to 0.65 nm, the particle size applying for the zeolite which is used as adsorbent.

Zeolites which have been subjected to dealumination in order to replace the Al_2O_3 in the lattice by SiO_2 , which thereby increases the modulus, are highly suitable. At the same time, this makes the polar forces weaker and thus the hydrophobicity of the zeolite is increased (W. Otten et al., Chem.-Ing. Tech. 64 (1992) No. 10, pp. 915 - 925).

It is within the spirit of the invention to use the zeolites both as a loose bed in adsorber columns or as a membrane, a combination of adsorption stage and membrane stage likewise being within the spirit of the invention.

The adsorption is effected at a pressure of at most 15 atm. at 21°C.

In one embodiment of the method according to the invention, pest control with SO_2F_2 is performed in closed containers or spaces. The SO_2F_2 -containing atmosphere present as a gas mixture (0.05 to 10% by volume SO_2F_2) of the containers or spaces is removed therefrom once fumigation has ended and is contacted with the adsorbents and/or the membranes to recover the SO_2F_2 . The air which is depleted in SO_2F_2 from the gas mixture can then be let off into the atmosphere.

In another embodiment, the gas mixture is passed over two or more adsorption stages and/or membrane stages.

The adsorbed sulphur oxyfluoride can be desorbed from the sorbent by increasing the temperature and/or reducing the pressure and be sent for re-use.

The regeneration of the adsorbents (desorption) takes place in known manner by supplying heat and/or lowering the pressure.

The desorption takes place in a temperature range from 20 to 300°C, preferably at a temperature >100 °C. It has proved beneficial to allow the desorption to take place at reduced pressure. In one embodiment, the adsorber column after heating is exposed to a technical vacuum of up to 10^{-3} bar for desorption.

If the gas mixture additionally contains impurities, purification by e.g. filtration or adsorption with other adsorbents may take place before the adsorption. It is likewise within the spirit of the invention, first to free the gas mixture of water, e.g. by drying with suitable drying

agents, and then to pass it through the adsorbers or membrane.

The apparatus for implementing the method according to the invention comprises at least one adsorber with a bed of zeolites having a modulus >10 , preferably >100 , a particle size >1 mm, preferably >2 mm, and a pore diameter of 0.4 to 0.7 nm, preferably 0.5 to 0.65 nm, and/or at least one membrane, consisting of or containing a zeolite having a modulus of 10, preferably 100 and a pore diameter of 0.4 to 0.7 nm, preferably 0.5 to 0.65 nm. A compressor is located before the adsorber or the membrane. The apparatus comprises at least one supply line for the gas mixture, a line for removing the gas into the atmosphere and also measuring, regulating and monitoring means.

In a preferred embodiment, it has proved beneficial to use at least two adsorber stages, which may each also comprise a plurality of adsorber columns, since they permit continuous operation if connected in parallel. The alternate operation of adsorption and desorption is ensured by suitable regulating and control means.

In one embodiment of the invention, the gas mixture to be separated is introduced into the adsorber stage by means of a pump or compressor via a supply line.

The number and capacity of the adsorbers depends on whether a gas with a high or low sulphur oxyfluoride content is to be treated. The capacity of the adsorbers can for example be increased by increasing the adsorber volume of the individual adsorber columns or by the number of adsorber columns.

Before the impoverished gas is let off into the atmosphere, the composition of the gas is analysed and

monitored by means of a monitoring means, preferably by means of an IR analysis means.

The invention will be explained in greater detail with reference to Figure 1.

Fig. 1 shows a diagram of a plant with parallel adsorber stages with 2 adsorber columns in each case connected in series. This plant is very compact and is suitable for construction on the loading surface for example of a heavy goods vehicle. For simplicity, the compressors before each adsorber column have been omitted. Likewise, the heating means, vacuum pumps, measuring and regulating devices etc. are not shown.

The adsorber columns are filled with a loose bed of the above zeolites.

The plant is laid out such that for continuous operation one adsorber line adsorbs and the other adsorber line is regenerated.

The gas mixture at a pressure of at most 20 bar (abs.) is introduced via line A into the adsorber 1. The gas mixture leaving the adsorber 1 is passed into the adsorber 2 via line B. Before the gas mixture leaving the adsorber 2, which contains no or only insignificant amounts of sulphur oxyfluoride, is discharged into the atmosphere, the composition of the gas mixture is analysed and monitored in the monitoring means AE (preferably an IR-analysis apparatus).

Simultaneously the adsorbers 3 and 4, which are connected to each other via line D, are regenerated, i.e. the adsorbed gas mixture is desorbed.

The desorption takes place by pressure, and change in temperature, in that the adsorber columns are heated and/or the pressure in the adsorber columns is changed with the aid of vacuum pumps.

The desorbed gas mixture which is greatly enriched with sulphur oxyfluoride is collected in the storage container and is thus available for further use.

In another embodiment of the method the gas to be separated passes through a combination of membrane separation stage and adsorption separation stage.

The pressure on the inlet side of the membrane is usually higher than the ambient pressure. A pump or a compressor is located before the membrane. The gas mixture to be separated is fed at a pressure of up to 20 bar. The retentate leaving the membrane stage, with an increased content of sulphur oxyfluoride, passes into a collecting container and can be re-used immediately e.g. after liquefaction with a compressor.

The permeate is passed into at least one adsorber for further separation. Optionally the permeate may be compressed before entry into the adsorber.

It is likewise conceivable that the retentate of the first membrane stage is introduced into a second membrane stage. The permeate resulting from this second membrane stage can be recycled into the first membrane stage or be passed into the subsequent adsorber stages.

The membrane may be present in conventional form. The membrane material contains or consists of a zeolite having a modulus >10 , preferably >100 , and a pore diameter of 0.4 to 0.7 nm, preferably 0.5 to 0.65 nm.

The apparatus can also be constructed in mobile form, for example on the loading surface of a motor vehicle, so that the method according to the invention can be carried out in situ.

The following examples are intended to explain the invention, without limiting its scope.

For the following examples, the following zeolites were used as adsorbents:

No.	Trade Mark	Type	Modulus	Particle size	Pore diameter nm
1	Zeocat PZ-2/400	ZSM5 Na form	400	2.5 mm	0.53 x 0.56; 0.51 x 0.55
2	Wessalith DAZ F 20	Pentasil MF	>1,000	2 mm	0.6
3	Sicolith 400	4A granules	2	1-2 mm	0.4
4	Grace 522	A	2.6	1.6-2.5 mm	0.5

Example 1:

An $\text{SO}_2\text{F}_2/\text{N}_2$ mixture with 2.47% by volume SO_2F_2 was passed over an adsorber which contained a bed of 320 g adsorbent.

Zeocat PZ-2/400 (manufacturer: Chemie Uetikon GmbH, Uetikon (Switzerland)) was used as adsorbent.

The gas mixture was passed over the adsorbent for 54 min. at a throughflow rate of 3.13 l/min. until a maximum emission concentration of SO_2F_2 of 20 ppmv was reached. The adsorption capacity was determined by differential weighing.

Result: 23.28 g gas was adsorbed, of which 18.78 g was SO_2F_2 .

Example 2:

An $\text{SO}_2\text{F}_2/\text{N}_2$ mixture with 2.47% by volume SO_2F_2 was passed over an adsorber which contained a bed of 360 g adsorbent. Wessalith DAZ F20 (manufacturer: Degussa AG) was used as adsorbent.

The gas mixture was passed over the adsorbent for 44 min. at a throughflow rate of 3.63 l/min. until a maximum emission concentration of SO_2F_2 of 147 ppm was reached after 51 min. The adsorber capacity was determined by differential weighing.

Result: 23.4 g gas was adsorbed, of which 17.73 g was SO_2F_2 .

Example 3: (Comparison example)

Test performed analogously to Example 1

Sicolith 400 (manufacturer: Solvay) was used as adsorbent.

Result: no measurable quantity of gas was adsorbed.

Example 4: (Comparison example)

Test performed analogously to Example 2.

Grace 522 (manufacturer: W. R. Grace, Nd. Worms) was used as adsorbent.

Result: no measurable quantity of gas was adsorbed.

The results show that with zeolites which do not meet the selection criterion according to the invention in terms of modulus, particle size and pore diameter, no adsorption of e.g. SO_2F_2 is possible.

Claims

1. A method for the recovery or separation of sulphur oxyfluorides from gas mixtures, wherein the gas mixture is passed over adsorbents or membranes, characterised in that the gas mixture is passed over at least one adsorption and/or membrane stage, containing or consisting of zeolites having a modulus >10 and a pore diameter of 0.4 to 0.7 nm, and the sulphur oxyfluorides which are separated off are available for use optionally after desorption or directly.
2. A method according to Claim 1, characterised in that a zeolite having a modulus >10 , a particle size >1 mm and a pore diameter of 0.4 to 0.7 nm is used as adsorbent.
3. A method according to Claim 1, characterised in that a zeolite having a modulus >100 , a particle size >2 mm and a pore diameter of 0.5 to 0.65 nm is used as adsorbent.
4. A method according to Claim 1, characterised in that the membrane contains or consists of a zeolite having a modulus >100 and a pore diameter of 0.5 to 0.65 nm.
5. A method according to Claim 1, characterised in that the adsorption is performed at a pressure of at most 20 atm (at 21°C).
6. A method according to Claim 1, characterised in that a sulphur oxyfluoride/air mixture having a sulphur oxyfluoride content of at least 5 ppmv or 20 mg/m³ is used.
7. A method according to Claim 1, characterised in that 2 or more adsorption and/or membrane stages are used.



8. A method according to Claim 1, characterised in that the sulphur oxyfluorides are desorbed from the solvent by increasing the temperature and/or reducing the pressure.

9. A method according to Claim 8, characterised in that the desorption takes place in a temperature range from 20°C to 300°C, preferably at a temperature >100°C.

10. A method according to Claim 8, characterised in that the desorption takes place at a pressure of up to 10^{-3} bar.

11. A method according to Claims 1 to 10, characterised in that the method can be performed in a mobile apparatus.

