



G00002

1

30 JAN 2003

Separation of SF₆-containing gases



166166

Description

5

The invention relates to a process for the separation of gas mixtures which contain sulphur hexafluoride (SF₆).

- 10 SF₆-containing gases are used for widely varying purposes in industry. SF₆/N₂ mixtures or SF₆/noble gas mixtures and SF₆/air mixtures are used, for example, in the manufacture of windows as an insulating filler gas, and in the tyre industry as a pressure-resistant, noise-damping filler gas.
- 15 Mixtures of sulphur hexafluoride and nitrogen are used as an insulating filler gas for underground cables, see German Utility Model 297 20 507.2. Usually, these mixtures contain 5 to 30% by volume sulphur hexafluoride, remainder nitrogen to make up to 100% by volume.
- 20 Mixtures of sulphur hexafluoride and air and optionally CO₂ are used as a protective gas cushion when casting magnesium. SF₆ is usually contained in these mixtures in a quantity of 0.05 to 1% by volume.

SF₆-containing exhaust air may also occur in industry.

25

- It is desirable to work up these mixtures once they have been used, with the objective of re-using the SF₆. The problem is that nitrogen or air takes up a large volume percentage in the gas mixture, and requires a large transport capacity. It is an object of the present invention to devise a process for separating the above
- 30 gas mixtures which, when the SF₆ from the mixtures is re-used, requires only a small transport capacity.

A further object is to provide a suitable apparatus for performing the process

according to the invention.

In summary, a first aspect of the invention provides a process for separating SF_6/N_2 mixtures or SF_6/air mixtures, in which the mixture is contacted in at least one adsorption stage with hydrophobic zeolites having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm) in order preferentially to adsorb SF_6 and to recover N_2 depleted in SF_6 or air depleted in SF_6 .

In a second aspect of the invention provides an apparatus for separating SF_6/N_2 mixtures, comprising 1, 2, 3 or more membrane separation stages with membranes which are preferentially permeable to N_2 and 1, 2 or more adsorbers with a bed of zeolites having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm).

As mentioned, the process according to the invention for separating SF_6 -containing gas mixtures provides for the mixture to be contacted with hydrophobic zeolites having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ("modulus") of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm), in order to adsorb SF_6 preferentially. The substantially SF_6 -free nitrogen or the SF_6 -free air can be let off into the environment.

This simple way of performing the process is particularly suitable when relatively small quantities of gas mixture are to be separated or if the SF_6 content is low, e.g. below 5% by volume. It is therefore particularly well suited for the mixtures of SF_6 and air and optionally CO_2 which originate from the casting of magnesium and usually contain 0.05 to 1% by volume SF_6 . If additionally impurities such as SO_2F_2 , SO_2 etc. are contained therein, purification may be effected beforehand, such as washing with water or lye or sorption by means of e.g. Al_2O_3 . This way of performing the process is also well suited for separating filler gases from insulating panes and car tyres.

For example, the protective gas from the magnesium industry containing 0.2% by volume SF_6 , remainder air and CO_2 , is drawn off and the air is separated off. The

2a

sorbed SF_6 and CO_2 is recycled. With a few kilogrammes of adsorber material, virtually a whole week's production of exhaust gas from a melting crucible can be purified. Magnesium can therefore be produced in a far more environmentally friendly manner than previously. The desorption time is not longer, or even shorter, than the sorption time.

Although the SF_6 content is frequently 10% by volume for insulating-gas window panes, the extractor units frequently draw in secondary air, so that the effective SF_6 content is lower upon sorption.

One embodiment of the invention relates to a process for the purification of SF_6 -containing gases, in particular air or exhaust air contaminated with SF_6 .

This aspect of the invention is based on the finding that SF_6 can generally be separated out of gases using the selected zeolites.

Simple sorption tests show whether the separation occurs to the desired extent for
5 a particular gas from which SF_6 is to be removed. The separation effect is very successful if the molecules of the gas from which the SF_6 is to be separated are larger or smaller than the pore diameter of the zeolite used. In this manner, for example, gases from production can be purified.

10 The method can also be used for the purification of air or exhaust air which is contaminated with SF_6 .

The improvement according to the invention resides in effecting the purification of air or exhaust air which is contaminated with SF_6 .

15

If additional impurities such as SO_2F_2 , SO_2 etc. are contained therein, purification can be effected beforehand, such as washing with water or lye or sorption by means of, for example, Al_2O_3 .

20 The purification of the exhaust air, for example from plants in which SF_6 is produced or used, is effected on environmental grounds.

The purification of air containing SF_6 may be desirable because SF_6 may have a disruptive effect on industrial processes. One field of application is therefore the
25 purification of the air which is circulated in industrial plants.

The content of SF_6 in such air is frequently very low (in the range of parts per million). For this reason, it is usually possible to dispense with the provision of membrane separation beforehand. Furthermore, in view of the small quantities of
30 SF_6 , although it is possible to regenerate the laden sorbents, they may also be disposed of in the laden state.

To improve the purifying action, it is of course also possible to arrange a plurality of

adsorption stages (2, 3 or more) in series.

This embodiment according to the invention is distinguished by a high purifying action for air contaminated with SF_6 . The purified exhaust air or air can be let off
5 harmlessly into the environment or be passed harmlessly into plants in which SF_6 would have been a disturbing contaminant and serve as ambient air therein.

The process may for example also be applied to air or exhaust air to which SF_6 is added, e.g. as a tracer substance. Even air or exhaust air in plants manufacturing
10 or using SF_6 can be purified if this air or exhaust air is contaminated with SF_6 .

One preferred embodiment relates to the working-up of SF_6/N_2 mixtures, with reference to which the invention will be explained further.

15 If relatively large quantities are to be separated, or if the SF_6 is relatively large, the SF_6/N_2 mixture may first be subjected to low-temperature treatment. Preferably the mixture is cooled to a temperature in the range from -70°C to -110°C , in particular to a temperature in the range from -70°C to -100°C . SF_6 which only has a low content of N_2 then condenses out. Furthermore, a gas phase remains which
20 predominantly consists of nitrogen with low contents of SF_6 . The gas phase obtained in this manner is then separated by absorption as described above, so that nitrogen substantially free of SF_6 is obtained and can be let off into the environment. The SF_6 can be recycled.

25 An alternative, preferred embodiment for relatively large quantities of gas mixture, or those gas mixtures which have a higher content of SF_6 , will be described below. This embodiment provides for the combination of membrane separation processes and adsorption. It is highly suitable for mixtures of SF_6 and N_2 , for example from underground cables, which have an SF_6 content of 5 to 30% by volume.

30

This embodiment of the process according to the invention provides for an SF_6/N_2 mixture to be separated in at least one membrane separation stage into a retentate with an increased content of SF_6 and a permeate with a reduced content

of SF₆, and for the permeate to be passed into at least one adsorption stage with the hydrophobic zeolites described above for further separation. It is preferred to provide two or more membrane separation stages and two or more adsorption stages.

5

The pressure on the entry side of the membrane or membranes is usually greater than the ambient pressure. For example, the gas mixture to be separated may be supplied at a pressure of up to 2000 kPa (20 bar). If a plurality of membranes are provided, a compressor is arranged in front of each membrane. The permeate will
10 then usually have a pressure which corresponds approximately to the ambient pressure upon entry into the adsorber stage. If desired, the permeate may be compressed before entry into the adsorber stage. This is however not essential. It is simplest to feed the permeate into the adsorber stage at the pressure which results from the membrane. The pressure is then usually up to 400 kPa (4 bar) (absolute),
15 preferably up to 200 kPa (2 bar) (absolute).

If two membrane separation stages are provided, expediently the following guidance of the gas streams is provided: the mixture to be separated - for example, a mixture of sulphur hexafluoride and nitrogen containing 20% by
20 volume SF₆ from underground cables - is fed to the first membrane. Since the membrane preferentially allows nitrogen to pass, a permeate with a high nitrogen content and a low sulphur hexafluoride content is obtained. The permeate is introduced into the adsorber, or into the first adsorber; the gas mixture leaving the first adsorber is then introduced into a second, and then optionally into a third, etc.,
25 adsorber. Experiments have shown that after passing through just one membrane and two adsorbers filled with hydrophobic zeolites a nitrogen containing less than 10 ppm SF₆ is obtained. The retentate of the first membrane is introduced into an additional membrane. The permeate resulting from this second membrane is introduced into the first membrane. The retentate from the second membrane is
30 sulphur hexafluoride with small amounts of nitrogen. It can be stored temporarily after liquefaction with a compressor, be re-used immediately or be worked up, further enriching the sulphur hexafluoride.

The process may be performed very flexibly in terms of the number of membranes and adsorber stages. Depending on to what extent the depletion of SF₆ is to be effected, one, two or even more adsorber stages are provided.

- 5 The number of the membranes and the arrangement of the membrane cartridges will depend on whether a gas with a high or a low SF₆ content is to be treated. With a larger number of membranes, the separation effect is greater, and the SF₆ content in the permeate which is to be treated by adsorption is lower than when using a small number of membranes. The adsorber may then either be designed
- 10 to be smaller, or regeneration is necessary at longer intervals. The costs in terms of apparatus may however be higher (larger number of compressors).

- It has been established that even just one or two membrane separation stages and one or two adsorber stages are sufficient for a highly enriched sulphur
- 15 hexafluoride and a nitrogen gas with at most traces of sulphur hexafluoride to be obtained.

- Organic, asymmetrical membranes are preferred. As is known, there are rubber-elastic membranes ("rubbery membranes") which effect separation based on the
- 20 solubility of the permeate. Other membranes effect separation based on the diffusibility of the permeate; these are non-rubber-elastic, but rather crystalline, membranes ("glassy membranes"); these latter membranes are preferred. The membrane may be of conventional form. Membranes in the form of a bundle of hollow fibre membranes are highly suitable. The membrane material may consist,
- 25 for example, of polysulphone, polyetherimide, polypropylene, cellulose acetate, polyimide, polyamide, polyaramid or ethyl cellulose, as described in US-A 5,730,779. Other usable membranes are described in US-A 4,838,904. For example, polyimides, polycarbonates, polyesters, polyester carbonates, polysulphones, polyethersulphones, polyamides, polyphenylene oxides and
- 30 polyolefins are very highly suitable. Preferably the polymer material contains polyester, polycarbonates and polyester carbonates. Polycarbonates which have been derived from a biphenol in which at least 25% of the biphenol units in the polymer chain are tetrahalogenated, the halogen being chlorine or bromine, are

outstandingly suitable. Particularly preferred membranes have a polymeric matrix which has two porous surfaces and a layer which permits the separation of the sulphur hexafluoride from the other gas constituents. Such membranes are described in US Patent 4,838,904 (EP-A-0 340 262). If additional impurities such as SO_2F_2 , SO_2 etc. are contained in the gas mixture, purification may take place beforehand, such as washing with water or lye or with adsorbers. Each membrane stage may consist of a plurality of membrane cartridges (arranged in parallel).

The pressure on the entry side of the membrane or membranes is usually higher than the ambient pressure. For example, the gas mixture to be separated may be supplied at a pressure of up to 1300 kPa (13 bar). Preferably the entry pressure is from 1000 to 1200 kPa (10 to 12 bar). If a plurality of membranes are provided, a compressor may be arranged in front of each membrane. The temperature is advantageously from 10 to 40°C.

If three membrane stages are used, the separation effect is even better. Preferably the three membranes are connected as follows: the SF_6/N_2 gas mixture is fed as feed stream to the first membrane stage. The retentate is fed as feed stream to a second membrane stage. The retentate of this second stage is highly enriched SF_6 , and can be re-used. The permeate of the first membrane stage is fed as feed stream to the third membrane stage. The permeate of this third stage is N_2 , virtually free of SF_6 , and is let off into the environment after passing through the adsorber or adsorbers. The permeate of the second membrane stage and the retentate of the third membrane stage are introduced into the feed stream to the first membrane stage.

It was established that, with zeolites which do not meet the selection criterion according to the invention in terms of modulus and pore size, only poorer adsorption of sulphur hexafluoride or none at all is possible, or that they are substantially less selective. A pore diameter of 5 to 6.5 Å (0.5 to 0.65 nm) is particularly advantageous.

It is possible to regenerate the adsorbents by lowering the pressure (pressure alternation adsorption) and optionally allowing heat to act on the coated

adsorbents. The sulphur hexafluoride released may for example be fed to the feed stream into the membrane separation plant.

The process according to the invention is distinguished by optimum splitting of the
5 SF_6/N_2 mixture or SF_6/air mixtures. The purified nitrogen or the purified air may be let off harmlessly into the environment. The recovered sulphur hexafluoride may either be re-used immediately or after further purification - optionally in liquefied form. The apparatus to be used in the process according to the invention may be in mobile form. In this case, the gas mixture, which originates for example from
10 underground cables, may be separated on the spot.

The invention also covers an apparatus. This apparatus for separating sulphur hexafluoride/nitrogen or SF_6/air mixtures comprises one, two, three or more membrane separation stages with membranes which are preferentially permeable
15 to nitrogen or air, and one, two or more adsorbers with a bed of zeolites having a silicon dioxide/aluminium oxide ratio (modulus) of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm). What has been stated above applies with regard to the number of membrane and adsorber stages. A compressor is arranged before each membrane stage. A preferred apparatus, as explained in Figure 1, has two
20 membrane separation stages and two adsorber stages. It further comprises a feed line for the gas mixture to be separated, which line is connected to the inlet into the first membrane separation stage, a connecting line between the first and second membrane separation stages which is intended for introducing the retentate from the first membrane separation stage into the second membrane
25 separation stage, a connecting line between the second and first membrane separation stages, which serves for introducing the permeate of the second membrane separation stage into the first membrane separation stage, a line for removing the retentate from the second membrane separation stage, from which retentate with a high SF_6 content can be removed, a line for feeding the permeate
30 of the first membrane separation stage into the first adsorber, a line for feeding the gas leaving the first adsorber into the second adsorber and a line for removing the substantially SF_6 -free nitrogen gas (or SF_6 -free air) from the second adsorber.

A further, particularly preferred system comprises three membrane stages.

Expediently, they are connected as described further above. Figure 2 explains this in greater detail. Container B (symbolises the gas-insulated line) has a mixture of N_2 and SF_6 . The mixture is passed into the first membrane stage 2 through line 1.

- 5 The retentate is fed via line 3 into the second membrane stage 4. The retentate, highly enriched SF_6 , of membrane stage 4 is introduced via line 5 into the storage container V (intermediate tank). The permeate of the first membrane stage 2 is fed into a third membrane stage, the permeate of which can be introduced into the adsorber (or adsorbers). The retentate of the third membrane separation stage is
- 10 introduced via line 7 into the feed stream of the first membrane stage 2. The permeate of the second membrane stage 4 is also introduced, via line 9, into the feed stream of the first membrane stage 2. Compressors before the membrane stages, probes for analysing samples, flow meters etc. are omitted for the purpose of clarity.

15

Depending on the adsorber capacity and the number of membrane separation stages, merely one adsorber stage may also be provided. Two adsorber stages or more are advantageous, since they permit continuous operation if connected in parallel.

20

The apparatus may be arranged in mobile form, for example constructed on the loading surface of a motor vehicle (e.g. lorry). Then the process according to the invention can be carried out on the spot.

- 25 The invention will be explained in greater detail in relation to Example 1 with reference to Figure 1.

Example 1: Combination of membrane separation and sorption

- An installation with two membrane separation stages and two adsorbers
- 30 connected in series was used. This installation is very compact (space required: 9 metre (30-foot) container) and is suitable for construction on the loading surface for example of a lorry. For simplicity, the compressors before each membrane have been omitted.

The membranes used were of the hollow-fibre type, manufactured by Aga-Gas, type AVIR™. "Wessalith® DAZ F20", manufactured by Degussa, was used. This is a zeolite of the Pentasil type, which has been subjected to dealumination in order to replace the Al_2O_3 in the lattice with SiO_2 and in this manner to increase the modulus. This type of modification is also used with other zeolites in order to replace Al_2O_3 in the zeolite with SiO_2 . One method provides for contacting the zeolite with SiCl_4 for this purpose, cf. W. Otten, E. Gail and T. Frey, Chem.-Ing.-Tech. 64 (1992), No. 10, pages 915-925, in particular pages 915-916.

10

The zeolite used, "Wessalith® DAZ F20", has a modulus of over 1,000, a pore width of 0.6 nm and a particle size of 2 mm. 500 g of this adsorbent were used.

By mixing nitrogen and sulphur hexafluoride, a gas mixture containing 20% by volume SF_6 and 80% by volume N_2 was produced, which corresponds to a gas mixture used, for example, in underground cables. The gas mixture at a pressure of 1300 kPa (13 bar) (absolute) was introduced via line 1 into the first membrane separation stage 2 ($1 \text{ m}^3/\text{h}$). The permeate leaving the first membrane separation stage contained 97% by volume nitrogen and 3% by volume sulphur hexafluoride, and was introduced at approximately ambient pressure via line 8 into the first adsorber 9 and the gas mixture leaving the adsorber was introduced via line 10 into the second adsorber 11. A gas which contained less than 10 ppm sulphur hexafluoride was removed via line 12.

The retentate of the first membrane separation stage contained 50% by volume nitrogen and 50% by volume sulphur hexafluoride and was introduced into the second membrane separation stage 4 via line 3 after it had been compressed to 1300 kPa (13 bar). The permeate from the second membrane separation stage contained 81% by volume nitrogen and 19% by volume sulphur hexafluoride, and was returned to the first membrane separation stage via line 5. The retentate of the second membrane separation stage contained 95% by volume sulphur hexafluoride and 5% by volume nitrogen. It was introduced into a storage container 7 via line 6. This product is so pure that it can be used directly for re-

using the SF_6 . If desired, however, it may also be purified further.

Example 1 was repeated, this time with 3 membranes. The permeate leaving the third membrane still contained 1% by volume SF_6 before being passed into the
 5 adsorber. The intervals before regeneration are correspondingly longer.

Examples 2 to 13:

12 zeolites were investigated in terms of their suitability as adsorbents for
 10 separating SF_6/N_2 mixtures. An SF_6/N_2 mixture containing about 1% by volume
 SF_6 was passed over two adsorbers connected in series, which contained a bed of
 500 ml of the respective adsorbent. The mixture was passed through until about
 10 g SF_6 had been passed through. The mixture leaving the second adsorber was
 investigated using gas chromatography, and the SF_6 concentration was determined.
 15 The first series of tests was carried out at ambient pressure (100 kPa) (1 bar).

The adsorbents investigated, their characteristics and an evaluation of their
 adsorptive capacity are summarised in the following table. Therein, zeolite No. 1
 corresponds to Example 2, etc.

20

** Manufacturers: No. 1, No. 4: Degussa AG;
 No. 5: Bayer AG, Leverkusen;
 No. 3, No. 7, No. 8: Chemie Uetikon GmbH, Uetikon
 (Switzerland);
 25 No. 2: Sued-Chemie, Munich;
 No. 6: W.R. Grace, Nd. Worms;
 No. 9: Solvay; No. 10: UOP, Nd. Erkrath;
 No. 11: Atochem Deutschland, Nd. Düsseldorf;
 No. 12: Zeoline, Engis (Belgium)

30

- 1) Adsorber 1, measured after 5 min.
- 2) Adsorber 2, measured after 10 min.
- 3) Used as extrudate

Table 1: Zeolites Investigated

Zeolite No.	Trade Name	Type	Modulus	Pore diameter [nm]	Particle size	Concentration of SF ₆ (mg/l) after absorber		Observations
						1 ¹⁾	2 ²⁾	
1	Wessalith DAZ F20	Pentasil MFI	> 1,000	0.6	2 mm	12.56	10.52	
2	T 4480	Pentasil ZSM5	90	0.58	> 1µm ³⁾	1.62	0.38	
3	Zeocat PZ-2/400	ZSM 5, Na form	400	0.53 x 0.56; 0.51 x 0.55	2 - 5 mm	11.48	0.23	
4	Wessalith DAY F20	Y-zeolite (FAU)	>200	0.8	2 mm	60.98	61.23	Comparison example
5	Baylith WE 894	X in Na form	2.5	0.9	2 - 4 mm	56.02	46.08	Comparison example
6	Grace 522	A	2.6	0.5	1.6 - 2.5 mm	61.93	28.82	Comparison example
7	Zeocat FM-8	Mordenite SM	12	0.26 - 0.57; 0.65 - 0.7	1 - 2 µm	61.16	62.26	Comparison example
8	Zeocat 6-08-02	Y-zeolite	5-6	0.74	2.45 nm	41.64	56.57	Comparison example
9	Sicolith	4A-granules	2	0.4	1 - 2 mm	61.37	61.21	Comparison example
10	Molsieb 13x UOP	Y-type, Na form	1-2	1.0	1.45 - 2 mm	1.91	35.19	Comparison example
11	ATO Siliporite G5	X-type, Na form	1.25	1.0	1.5 - 1.85 mm	54.82	56.82	Comparison example
12	Zeoline	Na form	2	0.4	2.7 µm	25.91	55.21	Comparison example

For manufacturers: see ** page 9

The table shows that zeolites having a modulus of >80 and a pore width of 4 to 7 nm display a good adsorptive capacity even at ambient pressure.

It was observed that for the adsorbents suitable for the process according to the
5 invention the adsorption of SF_6 is improved, but the adsorption of N_2 is reduced, if the pressure is increased; the selectivity therefore increases. However, higher costs in terms of apparatus are incurred.

Examples 2-4 and 6 (zeolites Nos. 1 - 3 and 5) were repeated at a pressure of 200, 300
10 and 400 kPa (2, 3 and 4 bar). Zeolite No. 3 displayed such good values even at 100 kPa (1 bar) that they were not improved further by operating under pressure. The other zeolites displayed an improvement in the adsorption.

Further tests at an SF_6 concentration of 2 and 4% by volume showed that in this
15 case too zeolite No. 3 yielded the best results.

1. A process for separating SF_6/N_2 mixtures or SF_6 /air mixtures, in which the
5 mixture is contacted in at least one adsorption stage with hydrophobic zeolites having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm) in order preferentially to adsorb SF_6 and to recover N_2 depleted in SF_6 or air depleted in SF_6 .
- 10 2. A process according to Claim 1, characterised in that hydrophobic zeolite having a pore diameter of 5 to 6.5 Å (0.5 to 0.65 nm) is used.
3. A process according to Claim 1, characterised in that the adsorption is performed at a pressure of at most 507 kPa (5 atm) (absolute).
- 15 4. A process according to Claim 1, characterised in that the process is used for separating off SF_6 from SF_6 -containing gases.
5. A process according to Claim 1, characterised in that SF_6 -containing
20 exhaust air or exhaust gases, exhaust gases from the magnesium industry, insulating gas from window panes or filler gas from tyres is used.
6. A process according to Claim 1, characterised in that the mixture is first separated in at least one membrane separation stage into a retentate having an
25 increased content of SF_6 and a permeate having a reduced content of SF_6 and the permeate for further separation in at least one adsorption stage is contacted with hydrophobic zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm) in order preferentially to adsorb SF_6 .
- 30 7. A process according to Claim 1 or 6, characterised in that the starting point is an SF_6/N_2 mixture having an SF_6 content of 5 to 30% by volume or an SF_6 /air mixture of 0.05 to 2%.
8. A process according to Claim 6 or 7, characterised in that two or more
35 membrane separation stages and two or more adsorption stages are provided.

9. A process according to Claim 8, characterised in that two membrane separation stages are provided, the retentate of the first membrane separation stage is fed to the second membrane separation stage in order to obtain a mixture having an increased SF₆ content as retentate from the second membrane separation stage, the permeate of the second membrane separation stage is returned into the first membrane separation stage with an increased N₂ content or air content and the permeate of the first membrane separation stage with a high N₂ content or air content is fed to one, two or more adsorber stages in order to obtain N₂ or air with a greatly depleted SF₆ content.
10. A process according to Claim 9, characterised in that two adsorber stages are provided in order to obtain N₂ or air with less than 10 ppm SF₆ at ambient pressure.
11. An apparatus for separating SF₆/N₂ mixtures, comprising 1, 2, 3 or more membrane separation stages (2,4) with membranes which are preferentially permeable to N₂ and 1, 2 or more adsorbers (9,11) with a bed of zeolites having an SiO₂/Al₂O₃ ratio of at least 80 and a pore diameter of 4 to 7 Å (0.4 to 0.7 nm).
12. An apparatus according to Claim 11 with 2 membrane separation stages and 2 adsorber stages, comprising a line (1) for feeding the gas mixture to be separated into the first membrane separation stage (2), a connecting line (3) for the retentate for introduction into the second membrane separation stage (4), a connecting line (5) between the second (4) and first (2) membrane separation stages for introducing the permeate of the second membrane separation stage (4) into the first membrane separation stage (2), a line (6) for removing the retentate from the second membrane separation stage (4) with high SF₆ content, a line (8) for feeding the permeate of the first membrane separation stage (2) into the first adsorber (9), a line (10) for feeding the gas leaving the first adsorber (9) into the second adsorber (11) and a line (12) for removing the substantially SF₆-free N₂ gas from the second adsorber (11).
13. An apparatus according to Claim 12, comprising a third membrane separation stage (6) with a connecting line (10) for the permeate of the third membrane separation stage (6) for introduction into the adsorber, a connecting line (7) for introducing the retentate of the third stage into the first membrane separation stage (2), a connecting line (8) for introducing the permeate of the first membrane separation stage (2) into the third

membrane separation stage (6) and a connecting line (9) for introducing the permeate of the second membrane separation stage (4) into the first membrane separation stage (2).

14. An apparatus according to one of Claims 11 to 13 in mobile form, for example
5 constructed on board a motor vehicle.