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Separating off SF_6 from insulating gases
from gas-insulated lines

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Description

The invention relates to a process for separating mixtures which comprise sulphur hexafluoride (SF_6) and nitrogen (N_2) and originate from gas-insulated lines ("GIL").

Mixtures of sulphur hexafluoride and nitrogen are used as insulating filler gas for underground cables, see German Utility Model 297 20 507.2. Usually, these mixtures comprise from 5 to 50% by volume of sulphur hexafluoride, and the remainder to 100% by volume nitrogen.

In the context of servicing the lines, or in the event of faults, separating the gas mixture is desirable, in particular for the purpose of reusing the SF_6 . The SF_6 thus produced then occupies a very small volume (advantage during transport, design of line cross sections etc.).



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EP 0 853 970 and EP 0 754 487 describe a process for separating gas mixtures which are produced in the manufacture of semiconductors. Such gas
5 mixtures may contain perfluoro compounds. The separation of the gas mixtures is effected using membranes. US 5,843,208 describes a process for recovering SF₆ from gas mixtures using membranes at a pressure of at most 6.2 bar.

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The object of the present invention is to specify a process for separating the abovementioned gas mixtures which makes it possible to isolate the SF₆ from the mixtures for the purpose of reintroduction into the gas-insulated line or reuse in the context of a closed product cycle.

A further object is the provision of a suitable apparatus.

The process of the invention provides that SF₆/N₂ mixtures originating from gas-insulated lines are separated by means of membranes

which are able to separate off sulphur hexafluoride. The process of the invention can be carried out, for example, during the servicing of gas-insulated high-voltage lines, in the event of faults or if it has
5 proved that the gas in the line requires regeneration. The sulphur hexafluoride separated off can be recycled into the gas-insulated line. Depending on the concentration desired, nitrogen is then also introduced into the line. Another possibility of use is working up
10 appropriately in the process of the invention the mixtures of SF_6 and N_2 (and any other impurities) which are situated in the gas-insulated line, when the use of the gas-insulated line is terminated and this line is to be scrapped. The SF_6 can be isolated from the
15 mixtures and supplied for reprocessing.

The SF_6 content is in the range from 5 to 50% by volume. However, the process of the invention can also be applied to separating gas mixtures having a higher SF_6 content.

20 Preference is given to organic, asymmetric membranes. Rubbery membranes are known which separate on the basis of the solubility of the permeate. Other membranes separate on the basis of the diffusion property of the permeate; these are non-rubbery
25 membranes, or rather crystalline membranes ("glassy membranes"); preference is given to these latter membranes.

The membrane can be made up in a known manner, for example as a bundle of hollow-fibre membranes. The
30 membrane can be produced from known materials. Those which are very highly suitable are, for example, polyimides, polycarbonates, polyesters, polyester-carbonates, polysulphones, polyethersulphones, polyamides, polyphenylene oxides and polyolefins.
35 Preferably, the polymer material comprises polyesters, polycarbonates and polyester-carbonates. Those which are outstandingly suitable are polycarbonates which are derived from a bisphenol in which at least 25% of the bisphenol units in the polymer chain are

tetrahalogenated, wherein the halogen is chlorine or bromine. Particularly preferred membranes have a polymeric matrix which has two porous surfaces and one layer which makes it possible to separate the sulphur hexafluoride from the other gas constituents. Membranes of this type 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 present in the gas mixture, purification can be carried out in advance, such as washing with water or a lye or with adsorbers. Each membrane stage can consist of a plurality of membrane cartridges (disposed in parallel).

The pressure on the inlet side of the membrane or membranes is customarily higher than the ambient pressure. For example, the gas mixture to be separated can be fed at a pressure of up to 13 bar. Preferably, the inlet pressure is from 10 to 12 bar. If a plurality of membranes are provided, a compressor can be disposed upstream of each membrane. The temperature is advantageously at from 10 to 40°C.

If two membrane separation stages are provided, expediently the gas streams are conducted in the following manner: the mixture to be separated - for example a mixture of sulphur hexafluoride and nitrogen containing 20% by volume of SF_6 from gas-insulated high-voltage lines - is fed to the first membrane. Since the membrane lets nitrogen pass through preferentially, a permeate having a high nitrogen content and a low sulphur hexafluoride content is obtained. The permeate is discharged into the environment. The retentate of the first membrane - having an already high SF_6 concentration - is introduced into a further membrane. The permeate resulting from this second membrane is introduced into the feed stream of the first membrane. The retentate from the second membrane is sulphur hexafluoride having low amounts of nitrogen. It can, after liquefaction by a compressor, be recycled immediately into the gas-

insulated high-voltage line or be stored temporarily and reused in other ways.

The number and disposition of the membrane cartridges depends on the desired degree of purity and on whether a gas having high or low SF_6 content is to be treated. When three membrane stages are employed, the separation effect is better still. Preferably, the three membranes are connected as follows: the SF_6/N_2 gas mixture is fed to the first membrane stage as feed stream. The retentate is fed to a second membrane stage as feed stream. The retentate of this second stage is highly enriched SF_6 and is reprocessable. 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 discharged into the environment. 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 has been found that even one or two membrane stages are sufficient to be able to obtain a sufficiently enriched, purified sulphur hexafluoride and a nitrogen gas having acceptably low amounts of sulphur hexafluoride. A downstream adsorption stage is not provided.

The process of the invention is distinguished by excellent splitting of the SF_6/N_2 mixture from underground cables. The purified nitrogen and the purified air can be safely discharged into the environment. The emission of SF_6 into the environment is greatly decreased. The recovered sulphur hexafluoride can be introduced immediately back into the gas-insulated high-voltage line. However, other operations can also be performed, for example admixing nitrogen, in order to obtain the desired gas mixture.

The invention also relates to a system comprising a gas-insulated, SF_6/N_2 -filled [gas-insulated] high-voltage line, a membrane separation plant and connection lines between the gas-insulated

high-voltage line and the membrane separation plant.

The membrane separation plant comprises one, two, three or more membrane separation stages having membranes which are preferentially permeable to nitrogen. The

5 above applies to the number of membrane stages.

Upstream of the first membrane stage, and preferably upstream of each other membrane stage, is disposed one compressor. A preferred plant has at least two membrane separation stages. It further comprises a connection

10 line for the gas mixture to be separated, which connection line is connected to the gas-insulated high-voltage line and to the inlet into the first membrane separation stage, a connection line between the first and second membrane separation stages, which line is

15 provided for introducing the retentate (enriched with SF_6) from the first membrane separation stage into the second membrane separation stage, a takeoff line for the retentate from the second membrane separation stage, from which retentate having a high SF_6 content

20 can be taken off. This takeoff line connects the membrane separation plant to the gas-insulated high-voltage line (connection line for recycling the SF_6) or a tank for temporary storage. In addition, the plant has a return line for feeding the permeate of the

25 second membrane stage into the feed stream of the first membrane stage. Pumps (for example vacuum pumps) and compressors for withdrawing and feeding in the gas mixture or SF_6 are provided between the gas-insulated line and membrane separation plant. If desired, other
30 treatment devices can be connected intermediately (compressor, gas mixer for N_2 admixture etc.). The permeate of the first membrane stage can be discharged into the environment.

A further particularly preferred system
35 comprises three membrane stages. Expediently, they are connected as described above. Vessel B (symbolises the gas-insulated line) has a mixture of N_2 and SF_6 . The mixture is passed via line 1 into the first membrane stage 2. The retentate is fed via line 3 into the

second membrane stage 4. The retentate, highly enriched SF_6 , of the membrane stage 4 is introduced via line 5 into the storage vessel V (buffer tank). The permeate of the first membrane stage 2 is fed into a third
5 membrane stage, the permeate of which can be discharged into the environment (via line 10) and the retentate is introduced via the line 7 into the feed stream of the first membrane stage 2. The permeate of the second membrane stage 4 is also introduced into the feed
10 stream of the first membrane stage 2 via line 9. Compressors upstream of the membrane stages, probes for sample analysis, flow meters etc. have been omitted for the sake of clarity. The numbers serve to describe Example 2. They specify the volumetric ratio of N_2/SF_6
15 in the respective line.

The invention makes possible in a simple manner the reprocessing of the SF_6 content in gas-insulated lines.

The examples hereinafter are intended to
20 describe the invention further without restricting it in its scope.

The membranes used were of the hollow fibre type, manufacturer: Aga-Gas, type NitroprineTM; 3 cartridges per membrane separation stage.

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Example 1:

Two-stage process

Nitrogen and sulphur hexafluoride were mixed to generate a gas mixture containing 20% by volume of SF_6
30 and 80% by volume of N_2 , which corresponds to a gas mixture used in underground cables. The gas mixture, which was pressurised to 13 bar (absolute), was introduced ($1 \text{ m}^3/\text{h}$) via the line 1 into the first membrane separation stage 2 from a vessel B which
35 corresponds to the gas-insulated line. The permeate leaving the first membrane separation stage comprised 97% by volume of nitrogen and 3% by volume of sulphur hexafluoride.

The retentate of the first membrane separation stage comprised 50% by volume of nitrogen and 50% by volume of sulphur hexafluoride and, after recompression to 13 bar, was introduced via the line 3 into the second membrane separation stage 4. The permeate from the second membrane separation stage comprised 81% by volume of nitrogen and 19% by volume of sulphur hexafluoride. The retentate of the second membrane separation stage comprised 95% by volume of sulphur hexafluoride and 5% by volume of nitrogen. It was introduced via the line 5 into a storage vessel V. This product is so pure that it can be used directly for reusing the SF_6 .

15 Example 2:

Process with three membranes

Example 1 was repeated, this time with three membranes, in accordance with Fig. 1.

The gas mixture to be treated was fed to the first membrane stage, the retentate of which was fed to the second membrane stage; its retentate was highly enriched SF_6 (95% by volume, remainder N_2) and could be used for reprocessing.

The permeate of the third membrane stage comprised only 1% by volume of SF_6 . The retentate was admixed (via line 7) to the feed stream to the first membrane stage.

- 8 -

claims

1. Process for separating SF_6/N_2 mixtures using membranes suitable for separating off SF_6 , characterised in that SF_6/N_2 mixtures from gas-insulated lines, having an SF_6 content of from 5 to 50% by volume, are separated at a membrane inlet pressure of 10 to 13 bar in a mobile membrane separation device, the membrane of which consists of a polymer matrix based on polycarbonate that is derived from a bisphenol in which at least 25% of the bisphenol units in the polymer chain are tetrahalogenated with chlorine or bromine.
2. Process according to Claim 1, characterized in that two or more membrane separation stages are provided.
3. Process according to Claim 2, characterized in that three membrane separation stages are provided, the retentate of the first membrane separation stage is fed to the second membrane separation stage in order to produce from the second membrane separation stage as retentate a mixture having a high SF_6 content, and the permeate of the first membrane stage is introduced into the third membrane stage and the permeate of the second membrane separation stage and the retentate of the third stage are recycled into the feed stream of the first membrane stage and the permeate of the third stage can be discharged into the environment.
4. Process according to Claim 1, characterized in that the process is employed during the use of the gas-insulated line for purifying the insulating gas mixture of SF_6 and N_2 or is employed for the purpose of reprocessing after use of the gas-insulated line has been terminated.

- 9 -

5. System comprising a gas-insulated line, a membrane separation device and one or more connection lines between the gas-insulated line and the membrane separation device, usable as a mobile membrane separation device.