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(54) Titre : SEPARATION DE SF₆ CONTENU DANS DES GAZ ISOLANTS PROVENANT DE LIGNES A ISOLATION GAZEUSE

(54) Title: ISOLATION OF SF₆ FROM INSULATING GASES IN GAS-INSULATED LINES

(57) Abrégé/Abstract:
Gas mixtures of SF₆ and N₂ which have been used as an insulating filler gas for underground cables can be split by means of a membrane separating off SF₆.
Abstract

Gas mixtures of \( \text{SF}_6 \) and \( \text{N}_2 \) which have been used as an insulating filler gas for underground cables can be split by means of a membrane separating off \( \text{SF}_6 \).
SEPARATING SF₆ FROM INSULATING GASES
FROM GAS-INSULATED LINES

The invention relates to a process for separating mixtures which comprise sulfur hexafluoride (SF₆) and nitrogen (N₂) and originate from gas-insulated lines ("GIL").

Mixtures of sulfur hexafluoride and nitrogen are used as insulating filler gas for underground cables. Usually, these mixtures comprise from 5 to 50% by volume of sulfur 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 SF₆. The SF₆ thus produced then occupies a very small volume (advantage during transport, design of line cross sections etc.).

EP 0 853 970 and EP 0 754 487 describe a process for separation of gas mixtures, which arise during the manufacture of semiconductors. Gas mixtures of this type may contain perfluoro compounds. The separation of the gas mixtures takes place at membranes. US 5,843,208 describes a process for the recovery of SF₆ from gas mixtures with the use of membranes at a pressure of at most 6.2 bar.

An 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 mixture for the purpose of reintroduction into the gas-insulated line or the reuse in the context of a closed product cycle.

Another object is to a suitable apparatus.

More specifically, the invention as claimed is directed to a process for separation of SF₆/N₂ mixtures with the use of membranes suitable for the
separation of SF₆, characterized in that, in a mobile membrane separating apparatus, the membranes of which consist of a polymer matrix composed of polycarbonate, which is made from a bisphenol, in which at least 25% of the bisphenol units in the polymer chain are tetrahalogenated with chlorine or bromine, SF₆/N₂ mixtures from gas insulated lines having a SF₆ content of from 5 to 50 volume % are separated at a membrane inlet pressure of 10 to 13 bar.

The process of the invention provides that SF₆/N₂ mixtures originating from gas-insulated lines are separated by means of membranes
event of faults or if it is 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 also introduced into the line. Another possibility of use is working up appropriately in the process of the invention mixtures of SF₆ and N₂ (with or without 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 SF₆ can be isolated from the mixtures and supplied for reprocessing.

The SF₆ 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 SF₆ content.

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 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 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. Preferably, the polymer material comprises polyesters, polycarbonates and polyestercarbonates. 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 $\text{SO}_2\text{F}_2$, $\text{SO}_2$ etc. are present in the gas mixture, a purification can be carried out in advance, such as washing with water or alkali metal hydroxide solution 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 $\text{SF}_6$ 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 $\text{SF}_6$ 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 according to whether a gas having high or low SF₆ content is to be treated. When three membrane stages are employed, the separation effect is still better. Preferably, the three membranes are connected as follows: the SF₆/N₂ 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 SF₆ 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 N₂, virtually free of SF₆, 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 SF₆/N₂ mixture from underground cables. The purified nitrogen and the purified air can be safely discharged into the environment. The emission of SF₆ 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, SF₆/N₂-filled 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 abovementioned 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 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 provided for introducing the retentate (enriched with SF₆) 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 SF₆ content can be taken off. This takeoff line connects the membrane separation plant to the gas-insulated high-voltage line (connection line for recycling the SF₆) or a tank for temporary storage. In addition, the plant has a return line for feeding the permeate of the 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 SF₆ are provided between gas-insulated line and membrane separation plant. If desired, other treatment devices can be connected intermediately (compressor, gas mixture for N₂ admixture etc.). The permeate of the first membrane stage can be discharged into the environment.

A further particularly preferred system comprises three membrane stages. Expediently, they are connected as described above. Vessel B (symbolizes the gas-insulated line) has a mixture of N₂ and SF₆. 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 SF₆, 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 via line 8 into a third membrane stage 6, 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 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 N₂/SF₆ in the respective line.

The invention makes possible in a simple manner the reprocessing of the SF₆ content in gas-insulated lines.

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

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

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates an embodiment of the invention having three membrane stages as described herein (2, 4, 6: membrane stages; B: gas-insulated line; V: storage vessel).

Example 1:
Two-stage process

Nitrogen and sulphur hexafluoride were mixed to generate a gas mixture containing 20% by volume of SF₆ and 80% by volume of N₂, which corresponds to a gas mixture used in underground cables. The gas mixture, which was
pressurized to 13 bar (absolute), was introduced (1 m³/h) via the line 1 into the first membrane separation stage 2 from a vessel B which 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 SF₆.

Example 2:
Process having 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 rententate was highly enriched SF₆ (95% by volume, remainder N₂) and could be used for reprocessing.

The permeate of the third membrane stage comprised only 1% by volume of SF₆. The retentate was admixed (via line 7) to the feed stream to the first membrane stage.
WHAT IS CLAIMED IS:

1. Process for separation of SF₆/N₂ mixtures with the use of membranes suitable for the separation of SF₆, characterized in that, in a mobile membrane separating apparatus, the membranes of which consist of a polymer matrix composed of polycarbonate, which is made from a bisphenol, in which at least 25% of the bisphenol units in the polymer chain are tetrahalogenated with chlorine or bromine, SF₆/N₂ mixtures from gas insulated lines having a SF₆ content of from 5 to 50 volume % are separated at a membrane inlet pressure of 10 to 13 bar.

2. Process according to claim 1, characterized in that two or more membrane separation stages are provided.

3. Process according to claim 1, 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 obtain a mixture with a high SF₆ content as retentate from the second membrane separation stage, and the permeate of the first membrane separation stage is introduced into the third membrane separation stage, and the permeate of the second membrane separation stage and the retentate of the third membrane separation stage are recirculated to the feed stream of the first membrane separation stage, and the permeate of the third membrane separation stage can be released into the environment.

4. Process according to claim 1, characterized in that the process is utilized during the use of the gas insulated line to purify the insulating gas mixture of SF₆ and N₂ or after completed use of the gas insulated line for the purpose of reutilization.
5. A system for the separation of SF₆/N₂ mixtures comprising a gas insulated line, a membrane separation apparatus and one or more connecting lines between the gas insulated line and the membrane separation apparatus, said membrane separation apparatus being useful as a mobile membrane separation apparatus.
Fig. 1

1. 80/20
2. 80/20
3. 50/50
4. 5/95
5. 9/95
6. 97/3
7. 8/20
8. 80/20
9. 20 Vol.-% N₂
10. 99 Vol.-% N₂

N₂
SF₆