(12) STANDARD PATENT (11) Application No. AU 2012311500 B2
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Mixture of hydrofluoroolefin and fluoroketone for use as an insulation and/or arc-extinguishing medium and a gas insulated medium-voltage electrical device comprising same

(51) International Patent Classification(s)
H01H 33/22 (2006.01) ***H02B 13/055*** (2006.01)
C09K 3/30 (2006.01)

(21) Application No: **2012311500** (22) Date of Filing: **2012.09.21**

(87) WIPO No: **WO13/041695**

(30) Priority Data

(31) Number	(32) Date	(33) Country
11 58456	**2011.09.22**	**FR**

(43) Publication Date: **2013.03.28**
(44) Accepted Journal Date: **2017.04.06**

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(56) Related Art
DE 202009009305 U1
US 2010/0171062 A1
WO 2011/090992 A1
US 2010/0127209 A1

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
28 mars 2013 (28.03.2013)

WIPO | PCT

(10) Numéro de publication internationale
WO 2013/041695 A1

(51) Classification internationale des brevets :
H01H 33/22 (2006.01) *H02B 13/055* (2006.01)
C09K 3/30 (2006.01)

(21) Numéro de la demande internationale :
PCT/EP2012/068686

(22) Date de dépôt international :
21 septembre 2012 (21.09.2012)

(25) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :
11 58456 22 septembre 2011 (22.09.2011) FR

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(81) **États désignés** *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **États désignés** *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, RU, TJ, TM), européen (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Publiée :

— *avec rapport de recherche internationale (Art. 21(3))*

(54) **Title** : MIXTURE OF HYDROFLUOROOLEFIN AND FLUOROKETONE FOR USE AS AN INSULATION AND/OR ARC-EXTINGUISHING MEDIUM AND A GAS INSULATED MEDIUM-VOLTAGE ELECTRICAL DEVICE COMPRISING SAME

(54) **Titre** : MÉLANGE D'HYDROFLUOROOLÉFINE ET DE FLUOROCÉTONE POUR L'UTILISATION COMME MILIEU D'ISOLATION ET/OU D'EXTINCTION D'ARC ET APPAREIL ÉLECTRIQUE MOYENNE TENSION A ISOLATION GAZEUSE LE COMPRENANT

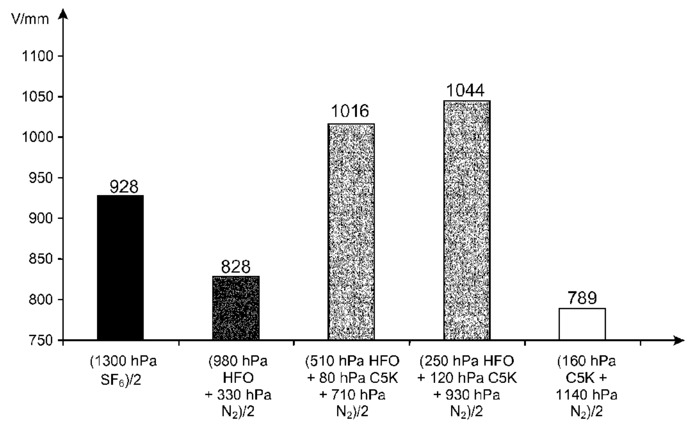

Fig.2B

(57) **Abstract** : The invention relates to the use of a mixture including a hydrofluoroolefin and a fluoroketone, optionally associated with a dilution gas, as an electric insulating and/or electric-arc-extinguishing medium in a medium-voltage electrical device. It also relates to a medium-voltage electrical device in which electric insulation and/or electric-arc-extinguishing is/are provided by a mixture comprising a hydrofluoroolefin and a fluoroketone, optionally associated with a dilution gas.

(57) **Abrégé** :

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WO 2013/041695 A1

L'invention se rapporte à l'utilisation d'un mélange comprenant une hydrofluorooléfine et une fluorocétone, éventuellement associées à un gaz de dilution comme milieu d'isolation électrique et/ou d'extinction des arcs électriques dans un appareil électrique moyenne tension. Elle se rapporte également à un appareil électrique moyenne tension dans lequel l'isolation électrique et/ou l'extinction des arcs électriques est (sont) assurée(s) par un mélange comprenant une hydrofluorooléfine et une fluorocétone, éventuellement associées à un gaz de dilution.

MIXTURE OF HYDROFLUOROOLEFIN AND FLUOROKETONE FOR USE AS AN INSULATION AND/OR ARC EXTINGUISHING MEDIUM AND A GAS INSULATED MEDIUM-VOLTAGE ELECTRICAL DEVICE COMPRISING SAME

DESCRIPTION

TECHNICAL FIELD

The present invention relates to the field of electrical insulation and extinguishing of electrical arcs in medium-voltage devices.

More precisely, it relates to the use of a mixture comprising a particular alkene, namely a hydrofluoroolefin with three carbon atoms, and a vector gas based on a fluoroketone, namely decafluoro-2-methylbutan-3-one, as an insulation and/or arc extinguishing medium in substation electrical devices and particularly in medium-voltage devices. The mixture may comprise other gases for which the global warming potential is lower, and particularly less than or equal to one.

It also relates to substation medium-voltage electrical devices in which the electrical insulation and/or electrical arc extinguishing are provided by a gaseous mixture comprising at least one fluoroketone and one hydrofluoroolefin, the latter compound having the highest global gas warming potential of the gases present in the gaseous medium.

Such an electrical device may notably be an electrical transformer such as a power supply or measurement transformer, a gas-insulated line for transporting or distributing electricity, a set of busbars or an electrical connection/disconnection device (also called a switchgear) such as a circuit breaker, a switch, a unit combining a switch with fuses, a disconnector, an earthing switch or a contactor.

STATE OF THE PRIOR ART

In the foregoing and what follows, the terms "medium-voltage" (MV) and "high-voltage" (HV) are used in their habitual acceptance, namely the term "medium-voltage" means a voltage that is greater than 1 000 volts for alternating current and 1 500 volts for direct current, but that does not exceed 52 000 volts for alternating current and 75 000 volts for direct current, while the term “high-voltage” refers to a voltage that is strictly greater than 52 000 volts for alternating current and 75 000 volts for direct current.

Electrical insulation and possibly extinguishing of electric arcs in medium- or high-voltage electrical devices are typically done by a gas confined inside an enclosure in the devices. At the present time, the most frequently used gas is sulphur hexafluoride (SF_6): this gas has a relatively high dielectric strength, a good thermal conductivity and low dielectric losses. It is chemically inert and non-toxic for humans and animals and, after being dissociated by an electric arc, it recombines quickly and almost entirely. It is also uninflammable and its price is still moderate.

However, SF_6 has the major disadvantage that it has a global warming potential (GWP) of 22 800 (relative to CO_2 over 100 years) and a residence time in the atmosphere of 3 200 years, which places it among gases having a strong global greenhouse effect. Therefore, SF_6 was included in the Kyoto Protocol (1997) on the list of gases for which emissions must be limited.

The best way to limit SF_6 emissions is to limit the use of this gas, which has led manufacturers to look for alternatives to SF_6. In fact, the other solutions such as hybrid systems combining a gas insulation with a solid insulation (EP 1 724 802 – reference **[1]**) increase the volume of the electrical devices relative to the volume that is possible with an SF_6 insulation; the cut off in oil or in a vacuum makes it necessary to redesign the devices.

Dielectric gases are known: see for example WO 2008/073790 (reference **[2]**). However, so-called “simple” gases like air or nitrogen, that have no negative impact on the environment, have a much lower dielectric strength than SF_6; their use for electrical insulation and/or extinguishing electrical arcs in HV/MV devices would require drastically increasing the volume and/or the filling pressure of these devices, which goes against efforts that have been made over the past few decades to develop compact and less bulky electrical devices.

Perfluorocarbons (C_nF_{2n+2}, c-C_4F_8) in general have attractive dielectric strength properties, but their GWP is typically within a range from 5 000 to 10 000. Other alternatives such as trifluoroiodomethane (CF_3I) that have promising electrical characteristics and GWP are classified among carcinogenic, mutagenic and reprotoxic substances of category 3, which makes them unacceptable for use on an industrial scale.

Mixtures of SF_6 and other gases such as nitrogen or nitrogen dioxide are used to limit the impact of SF_6 on the environment; see for example WO-A-2009/049144 (reference **[3]**). Nevertheless, due to the high GWP of SF_6, the GWP of these mixtures remains very high. Thus for example, a mixture of SF_6 and nitrogen with a ratio by volume of 10:90 has a dielectric strength in alternating current (50 Hz) equal to 59% of that of SF_6 but its GWP is of the order of 8 000 to 8 650. Therefore such mixtures cannot be used as a gas with a low environmental impact.

Thus, only mixtures with a high GWP have a dielectric strength similar to SF_6 at low temperature; all mixtures with low GWP known in the prior art can be used to reach not more than 80% of the performances of SF_6 devices for the lowest service temperatures; to come close to the performances of SF_6, these gaseous mixtures require a new design of the MV or HV devices taking account of longer insulation distances and possibly adding special devices such as screens, deflectors or cladding.

The inventors have thus set themselves the purpose of finding a gas which, while having good properties of electrical insulation and electrical arc extinguishing, has a low or zero impact on the environment. Research led them to envisage a new mixture of gases that can be used in currently marketed medium- or high-voltage electrical devices to replace the SF_6 with which such devices are generally filled, throughout their complete service temperature range and particularly at low temperatures.

Any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the invention. It should not be taken as an admission that any of the material formed part of the prior art base or the common general knowledge in the relevant art on or before the priority date of the claims herein.

Comprises/comprising and grammatical variations thereof when used in this specification are to be taken to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

PRESENTATION OF THE INVENTION

In one aspect, the invention proposes, firstly, the use of a gaseous medium comprising a hydrofluoroolefin with three carbon atoms and a fluoroketone with five carbon atoms as an electrical insulating and/or electric arc extinguishing medium in a sealed enclosure of substation medium-voltage electrical devices.

The fluoroketones used are ketones with a carbon chain having five carbon atoms, preferably totally substituted by fluorine and, even more preferably, of decafluoro-2-methylbutan-3-one type, which are not toxic, not corrosive, not explosive,

CONTINUES ON PAGE 4

which degrade very rapidly in the atmosphere due to the sensitivity of the -C=O double bond of the ketone group to ultraviolet and thus has a GWP close to 1.

The hydrofluoroolefins used are fluorinated alkenes with a carbon chain having three carbon atoms, preferably of $C_3H_2F_4$ or C_3HF_5 type, that are not toxic, not corrosive, not explosive, have an ODP (Ozone Depletion Potential) equal to 0, a GWP less than 10.

These two types of compound are provided with dielectric properties capable of allowing them to replace SF_6 as an insulation and/or arc extinguishing gas in substation medium-voltage electrical devices.

According to the invention, the mixture is such that its components are kept in the gas state under temperature and pressure conditions to which it will be submitted once it is confined in the electrical device. The mixture between fluoroketone and hydrofluoroolefin may thus be used alone; nevertheless, the mixture will most usually be diluted with at least one other gas that does not belong to their families, if the boiling point does not make it possible to guarantee it being maintained in the gaseous state at a total pressure sufficient for certain applications which, for example, may require more than 10^5 Pascals (Pa).

In this case, according to the invention, the other gases used in the gaseous medium have a lower global warming potential than hydrofluoroolefins; the vector gas, or dilution gas, or buffer gas, preferably has a very low boiling point, that is to say typically less than or equal to -50°C at the standard pressure, and a dielectric strength that is at least equal to the dielectric strength of nitrogen or carbon dioxide. Preferably, the mixture comprises a gas of nitrogen, air, advantageously dry air, oxygen, carbon dioxide type, or a mixture of these gases. The global GWP of the gaseous medium is relative to the partial pressures of each of its components and therefore less than 10, and preferably less than 5.

Advantageously, so as to place the maximum quantity of each of the gases without generating a liquid phase at the minimum service temperature of the device, the composition of the gaseous medium will be defined according to Raoult's law for the minimum service temperature of the device, or even for a temperature slightly above the latter, particularly 3°C above. In particular, for a ternary fluoroketone

(FK)/hydrofluoroolefin (HFO)/ dilution gas mixture, the pressures of each constituent will thus be defined by: $P_{total} = \frac{P_{HFO} + P_{FK}}{\frac{P_{HFO}}{PVS_{HFO}} + \frac{P_{FK}}{PVS_{FK}}} + P_{dilutiongaz}$, with PVS = saturated vapour pressure of the gas concerned. Thus, the dielectric properties of the gaseous medium in direct line and in tracking are the highest possible and which as far as possible approach those of SF_6.

In the preferred embodiments, the minimum service temperature T_{min} is chosen from: 0, -5, -10, -15, -20, -25, -30, -35, and -40°C. Advantageously, the partial pressure of fluoroketone is comprised between 80 and 120 hPa, particularly for a minimum service temperature of -25°C, with complement in HFO and N_2 according to Raoult's law applied at -22°C.

In another aspect of the invention there is provided a medium-voltage electrical device that comprises a sealed enclosure in which electrical components are located together with a gaseous medium providing electric insulating and/or extinguishing of electrical arcs likely to occur within said enclosure, the gaseous medium comprising a hydrofluoroolefin with three carbon atoms and a fluoroketone with five carbon atoms. The characteristics of the gaseous medium are as disclosed above with regard to its use. The device preferably comprises a $CaSO_4$ molecular sieve.

In accordance with the invention, this electrical device may be a gas-insulated electrical transformer such as, for example, a power supply transformer or a measurement transformer. The electrical device may also be a gas-insulated line, above ground or below ground, or a set of busbars for transporting or distributing electricity. Finally, it may also be an electrical connection/disconnection device (also called a switchgear) such as, for example, a circuit breaker, a switch, a disconnector, a unit combining a switch with fuses, an earthing switch or a contactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages and characteristics will become clearer from the following description of particular embodiments of the invention given for illustration and in no way limitative, represented in the appended figures.

Figures 1A and 1B show the saturated vapour pressure in a mixture according to a preferred embodiment of the invention as a function of the temperature: figure 1A illustrates the evolution of the total gas pressure for a ternary mixture, the proportions of which have been defined by Raoult's law for a theoretical appearance of liquid phase at -25°C, figure 1B for a theoretical appearance at -22°C.

Figure 2A represents a longitudinal section of the device for the tracking tests, the results of which are synthesised in figure 2B.

Figure 3A shows a device in which the dielectric strength tests in direct line have been carried out with a gaseous medium according to the invention, the results of which are synthesised in figure 3B.

Figure 4 synthesises the results obtained during partial discharge tests.

Figure 5 synthesises the results obtained during heating tests.

Figure 6 represents the saturated vapour pressure of two HFO and of C5K as a function of the temperature.

DETAILED PRESENTATION OF PARTICULAR EMBODIMENTS

The invention is based on the use, with or without dilution gas ("buffer" gas such as N_2, CO_2, air, etc.), of fluoroketones with five carbon atoms (C5K), and hydrofluoroolefins (HFO) with at least three carbon atoms. C5K are ketones substituted by fluorine, uninflammable and their GWP is very low; in particular, the C5K used have the empirical formula $C_5F_{10}O$, and, in particular, decafluoro-2-methylbutan-3-one is selected, which satisfies the semi-developed formula CF_3-CO-CF-$(CF_3)_2$, with a global warming potential GWP = 1. C5K are not toxic for humans with an occupational exposure limit (the average limit concentration to which most workers might be regularly exposed when working for 8 hours per day for 5 days per week, without being affected by any noxious effect) OEL = 1 000 ppm, and a lethal dose DL_{50} causing death of 50% of an animal population equal to more than 200 000 ppm.

HFO are alkenes substituted by fluorine with the general formula $C_n(H,F)_{2n}$; in particular, the HFO used comprise 3 carbon atoms; they are uninflammable and their GWP is less than 10. In particular, hydrofluoroolefin HFO-1234ze, or *trans*-1,3,3,3-tetrafluoro-1-propene, that satisfies the semi-developed formula CHF=CH-CF_3, is used for the following comparative examples. Its environmental impact is GWP = 6, and it is not toxic for humans with an OEL = 1 000 ppm and a DL_{50} > 200 000 ppm. Yet, in most conventional very low temperature applications (-30°C, or even -40°C), HFO is diluted, sometimes to less than 20 %, in a nitrogen type neutral vector gas: the mixture is thus not toxic. HFO-1234yf, or 2,3,3,3-tetrafluoro-1-propene, and HFO-1225ye, or 1,2,2,5-pentafluoro-1-propene, may also be envisaged for the mixture according to the invention.

According to the invention, the mixture of HFO and C5K is used in gaseous form regardless of the service temperature of the electrical device. Therefore, the partial pressure of each of these two components should be less than or equal to the pressure calculated according to Raoult's law. In fact, since the molecules of fluoroketones and hydrofluoroolefins are very similar by virtue of their composition, a limitation to their saturated vapour pressure for a given service temperature would generate a liquid phase at temperatures above the desired service temperature on account of interactions.

Depending on the device, the internal pressure of the insulation and/or arc extinguishing medium that is recommended varies; in particular, for different technical reasons, it is interesting to have a sufficiently high total pressure, generally strictly greater than 10^5 Pa. Since the HFO/C5K mixture is, according to the invention, entirely in gaseous form at the lowest temperature of the electrical device, to satisfy the given filling pressure conditions, a dilution gas, or buffer gas, is added if necessary. Preferably, the dilution gas has a very low boiling point, less than or equal to the minimum service temperature T_{min} of the device, and a dielectric strength greater than or equal to that of CO_2 or air in identical test conditions (same device, same geometric configuration, same operating parameters, etc.) to those used to measure the dielectric strength of said gas. Furthermore, according to the invention, the dilution gas used is a gas with low GWP of air or CO_2 type: thus, the gaseous medium used as insulation and arc extinguishing medium in electrical devices has a GWP less than or equal to that of the reference HFO. Preferably, for inhomogeneous field devices, carbon dioxide is used; alternatively, a dilution gas with zero GWP, nitrogen N_2, is used.

Advantageously, in order to maximise the quantity of each of the fluorinated gases constituting the mixture while not generating a liquid phase at the minimum service temperature of the device for a ternary fluoroketone C5K, hydrofluoroolefin HFO and dilution gas mixture, the pressures of each constituent will thus be defined by the following formula derived from Raoult's law (P_X being the pressure of the gas concerned and PVS_X its saturated vapour pressure):

$$P_{tot} = \frac{P_{HFO} + P_{C5K}}{\frac{P_{HFO}}{PVS_{HFO}} + \frac{P_{C5K}}{PVS_{C5K}}} + P_{dilutiongaz}$$

For example, for a minimum service temperature T_{min} = -25°C, several compositions of mixtures could be used to fill, without formation of liquid, an electrical device with sealed enclosure in which the total filling pressure at 20°C is 1.3 bars, in other words $1.3 \cdot 10^5$ Pa, as shown in table I below.

P_{C5K}	P_{HFO}	P_{N2}
$0.15 \cdot 10^5$ Pa	$0.05 \cdot 10^5$ Pa	$1.10 \cdot 10^5$ Pa
$0.14 \cdot 10^5$ Pa	$0.12 \cdot 10^5$ Pa	$1.04 \cdot 10^5$ Pa
$0.13 \cdot 10^5$ Pa	$0.18 \cdot 10^5$ Pa	$0.99 \cdot 10^5$ Pa
$0.12 \cdot 10^5$ Pa	$0.25 \cdot 10^5$ Pa	$0.93 \cdot 10^5$ Pa
$0.11 \cdot 10^5$ Pa	$0.31 \cdot 10^5$ Pa	$0.88 \cdot 10^5$ Pa
$0.10 \cdot 10^5$ Pa	$0.37 \cdot 10^5$ Pa	$0.83 \cdot 10^5$ Pa
$0.09 \cdot 10^5$ Pa	$0.43 \cdot 10^5$ Pa	$0.78 \cdot 10^5$ Pa
$0.08 \cdot 10^5$ Pa	$0.49 \cdot 10^5$ Pa	$0.73 \cdot 10^5$ Pa
$0.07 \cdot 10^5$ Pa	$0.55 \cdot 10^5$ Pa	$0.68 \cdot 10^5$ Pa
$0.06 \cdot 10^5$ Pa	$0.62 \cdot 10^5$ Pa	$0.62 \cdot 10^5$ Pa
$0.05 \cdot 10^5$ Pa	$0.68 \cdot 10^5$ Pa	$0.57 \cdot 10^5$ Pa
$0.04 \cdot 10^5$ Pa	$0.74 \cdot 10^5$ Pa	$0.52 \cdot 10^5$ Pa
$0.03 \cdot 10^5$ Pa	$0.8 \cdot 10^5$ Pa	$0.47 \cdot 10^5$ Pa
$0.02 \cdot 10^5$ Pa	$0.86 \cdot 10^5$ Pa	$0.42 \cdot 10^5$ Pa
10^3 Pa	$0.92 \cdot 10^5$ Pa	$0.37 \cdot 10^5$ Pa
10^2 Pa	$0.98 \cdot 10^5$ Pa	$0.319 \cdot 10^5$ Pa

Table I: proportions of a C5K + HFO-1234ze + N_2 mixture at $1.3 \cdot 10^5$ Pa

However it appears, by filling an enclosure equipped with a transparent window with such a mixture, there is only appearance of a liquid phase for these mixtures for a temperature less than or equal to -28°C: Raoult's law thus does not apply totally.

Yet, the dielectric strength of each of the two fluorinated compounds used in the mixture, pure HFO and pure C5K, is better than that of the dilution gas (see also figure 3B). Thus, to increase the dielectric properties of the mixture that derive directly from its molar composition, according to a preferred embodiment of the invention the mixture is optimised to include more fluorinated compound than the theoretical value above; advantageously, the theoretical composition is increased by an addition of C5K to improve the dielectric properties of the gaseous mixture, particularly in tracking, in proportions such that there is no appearance of liquid phase.

In particular, as shown in figure 1A, a mixture comprising 40 hPa of C5K, 740·hPa of HFO-1234ze and 520 hPa of nitrogen follows, at high temperature, more or less the curve defined by the perfect gas law; it diverges therefrom at low temperature, particularly below -28°C (and sometimes before due to the limits of use of the test devices at -20°C for example), corresponding to the cross-over with the curve illustrating the behaviour of this mixture according to Raoult's law. Consequently, at the lowest temperatures, respecting the values given by Raoult's law is more conservative and makes it possible to ensure the non-appearance of a liquid phase, the zone below the Raoult curve.

Thus, in figure 1B is shown the behaviour of the preceding mixture to which 20 hPa of C5K have been added; obviously, the curve is shifted proportionally below the perfect gas curve at high temperatures. If, theoretically, the appearance of liquid should occur at -22°C, experimentally (see also the break-off of the real curve) the formation of liquid occurs below -25°C.

According to a preferred embodiment of the invention, the composition of each of the components of the ternary mixture is determined by Raoult's law so that there is no appearance of liquid phase at a temperature that can be taken equal to the minimum operating temperature of the device or slightly higher, for example at said minimum temperature less 10 %, or preferably at the anticipated minimum service temperature plus 3°C.

The gaseous medium according to the invention satisfies the conditions of use of existing devices and its properties are superior to binary mixtures of each fluorinated gas, even SF_6, with synergetic effect between the two molecules of hydrofluoroolefin and fluoroketone. In particular, tracking strength tests have been carried out in a device at 1.3 ÷ 2 bars (in other words 1300 ÷ 2 hPa), shown in figure 2A, between two electrodes 251 mm apart, with copper conductors and a silica filled epoxy resin as insulator. As shown in figure 2B, it may be noted that the ternary mixtures constituted of HFO, C5K and a dilution gas according to the invention have a better tracking resistance than SF_6 (more than 1 000 V/mm compared to less than 930 V/mm) on the silica filled epoxide and than binary mixtures of each of the components (these constituents taken in isolation having properties inferior to SF_6).

Similarly, dielectric strength tests on a direct line at 1.3 bars (in other words 1300 hPa) show that the performances of the mixture according to the invention are greater than that of the individual components uniquely associated with a dilution gas: figure 3A shows the epoxide enclosure filled to 1.3 bars (i.e. 1300 hPa) with SF_6 or a mixture of N_2 with HFO and/or C5K to measure the dielectric strength between two contacts with a radius of 12 mm, at a distance of 12 mm. A synergetic effect between HFO and C5K is notable for the measured dielectric strength: figure 3B.

The advantage of a ternary mixture according to the invention compared to a binary mixture is also visible for partial discharges (figure 4): the extinction threshold is even greater than that at 65 kV of SF_6 for the ternary mixture, whereas it was lower for the binary mixtures.

In light of the performances of the fluorinated mixture according to the invention, alone or with a simple dilution gas of air or nitrogen type, a use in an existing device may be envisaged. In particular, after having created a vacuum (0 to 0.1 kPa) using an oil-filled vacuum pump, it is possible to fill a GIS type medium-voltage electrical device (the FBX 24 kV device of Schneider Electric for example, filled in its current commercial version with SF_6 at a pressure of 1300 hPa) designed for an application at -25°C with a mixture of C5K, HFO-1234ze and CO_2 gases, preferred in this case where the electric fields are not homogeneous. Furthermore, to avoid strikings between derivations, it is advantageous to sheath them with a heat-shrink sleeve.

The total pressure of gas inside the device with the mixture according to the invention is also chosen at 1.3 bars (P_{tot} = 1300 hPa) for 20°C, and the mixture satisfies the conditions defined by Raoult's law, for example with a partial pressure comprised between 80 and 120 hPa for C5K in so far as possible. Given the size of the enclosure of this device (volume greater than 100 litres), it is preferable, in order to speed up the homogenisation of the gaseous mixture, to use bubblers; obviously, this option is not obligatory, particularly in the case of smaller devices or sufficient delay before experimentation.

Furthermore, since apart from the improvement of the dielectric strength on a direct line, fluoroketones make it possible to improve the tracking dielectric strength of the system, it is preferable to adsorb it on the walls of the insulators. Firstly, to line the internal walls of the device with C5K, this compound is injected pure into the enclosure, for example between 3 and 10 hPa; advantageously between 80 and 120 hPa of C5K, preferably at a temperature above ambient temperature in order to speed up the flow rate (for example, the reservoir containing the C5K may be heated), are injected via the "gas" output of the device. After this first step enabling the fluoroketone to be adsorbed on the walls, the filling of the device takes place by means of a gas mixture with double bubbler making it possible to control the ratio between C5K, HFO-1234ze and CO_2, this ratio being maintained constant in pressure at 20°C throughout the filling thanks to the use of a precision mass flowmeter; for example, C5K is placed in the two bubblers through which CO_2 and the hydrofluoroolefin flow under pressure in order to attain complete saturation.

Tests on this type of device in which a permanent electrical current of 630 A RMS flows have shown that the heat at the level of the electrical contacts (the hottest points) is very similar to SF_6 for the ternary mixture according to the invention (as for binary mixtures): see figure 5, which gives the results in variation of the heating compared to SF_6.

Furthermore, it should be noted that the devices will be preferably equipped with one or more anhydrous calcium sulphate ($CaSO_4$) type molecular sieves, which absorb the small molecules created during the break. The toxicity of the gas is not increased after partial discharges by molecules that may have some toxicity.

Furthermore, at the end-of-life or after break tests, the gas is recovered using conventional recovery techniques using a compressor and a vacuum pump. Hydrofluoroolefin HFO-1234ze and fluoroketone C5K are then separated from the buffer gas using a zeolite capable of trapping only the buffer gas, smaller in size; alternatively, a selective separation membrane can allow nitrogen and/or CO_2 and/or air to escape and retains C5K and HFO-1234ze, which have a larger size and higher molecular mass; all other options could be considered.

Although the examples given above were made with HFO-1234ze, alternatives to this gas are possible. In particular, isomer HFO-1234yf (2,3,3,3-tetrafluoro-1-propene) can be used, with adaptations inherent to the properties of this gas: in particular, as shown in figure 6, since its boiling point is -30°C (compared with -19°C for HFO-1234ze), it is possible to use 50 % more HFO-1234yf than HFO-1234ze, for the same operating temperature of -30°C. Since for a given filling pressure, the more HFO there is, and consequently the less buffer gas there is, and since the insulation and arc extinguishing properties depend on the mixture, the dielectric strength is increased.

The solution according to the invention thus makes it possible to propose a gaseous mixture with a low environmental impact (GWP reduced by more than 99.9 % compared to an isolation with SF_6) compatible with the minimum service temperatures of the electrical device and with dielectric, break and thermal dissipation properties similar to what are obtained on existing devices. This mixture may directly replace the SF_6 used in the devices, without modifying or only slightly modifying their design: production lines can be kept, with simple change of filling gas and optionally with an addition of break aid systems or gas generating materials.

REFERENCES CITED

[1] EP 1 724 802

[2] WO 2008/073790

[3] WO 2009/049144

2012311500 09 Mar 2017

CLAIMS:

1. Use of a gaseous medium comprising a hydrofluoroolefin with three carbon atoms and a fluoroketone with five carbon atoms as an electric insulating and/or electric arc extinguishing medium in a sealed enclosure of substation medium-voltage electrical devices.

2. Use of a medium according to claim 1, in which the hydrofluoroolefin is *trans*-1,3,3,3-tetrafluoro-1-propene (HFO-1234ze), 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf), or 1,2,2,5-pentafluoro-1-propene (HFO-1225ye).

3. Use of a mixture according to claim 1 or claim 2, in which the fluoroketone is decafluoro-2-methylbutan-3-one.

4. Use according to any one of claims 1 to 3, in which the gaseous medium further comprises a dilution gas.

5. Use according to claim 4, in which the dilution gas is chosen from air, nitrogen, oxygen, carbon dioxide or a mixture of these gases.

6. Use according to any one of claims 1 to 5, in which the partial pressures of the fluoroketone and hydrofluoroolefin within the mixture are chosen as a function of the minimum temperature of the device so as not to create a liquid phase according to Raoult's law at a temperature of 3°C below the minimum service temperature of the device.

7. Use according to claim 6, in which the partial pressure of fluoroketone is comprised between 80 and 120 hPa.

8. Use according to claim 6 or claim 7, in which the minimum temperature (T_{min}) is chosen from -40°C, -35°C, -30°C, -25°C, -20°C, -15°C, -10°C, -5°C and 0°C.

9. Medium-voltage electrical device, comprising a sealed enclosure in which electrical components are located together with a gaseous medium providing electric

insulating and/or extinguishing of electric arcs likely to occur within said enclosure, wherein the gaseous medium comprises a hydrofluoroolefin with three carbon atoms and a fluoroketone with five carbon atoms.

10. Electrical device according to claim 9, in which the hydrofluoroolefin is *trans*-1,3,3,3-tetrafluoro-1-propene (HFO-12134ze) or 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf) or 1,2,2,5-pentafluoro-1-propene (HFO-1225ye), and the fluoroketone is decafluoro-2-methylbutan-3-one.

11. Electrical device according to claim 9 or claim 10, in which the gaseous medium further comprises a dilution gas.

12. Electrical device according to claim 11, in which the dilution gas is chosen from air, nitrogen, oxygen, carbon dioxide or a mixture of these gases.

13. Electrical device according to any one of claims 9 to 12, in which the hydrofluoroolefin and the fluoroketone are present in the medium with proportions defined according to Raoult's law so as not to create a liquid phase at a temperature of 3°C below the minimum service temperature of the device.

14. Electrical device according to any one of claims 9 to 13, which is a gas-insulated electrical transformer, a gas-insulated line for transporting or distributing electricity or an electrical connection/disconnection device.

15. Electrical device according to any one of claims 9 to 14, which comprises a $CaSO_4$ molecular sieve.

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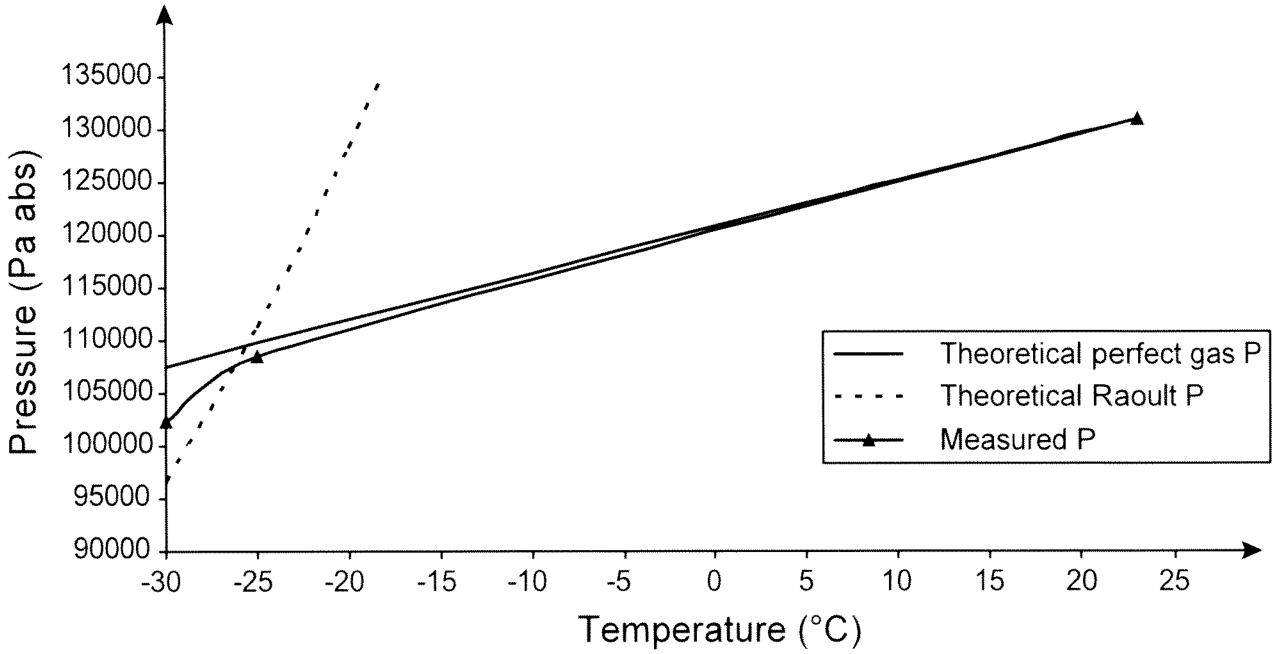

Pressure (Pa abs)
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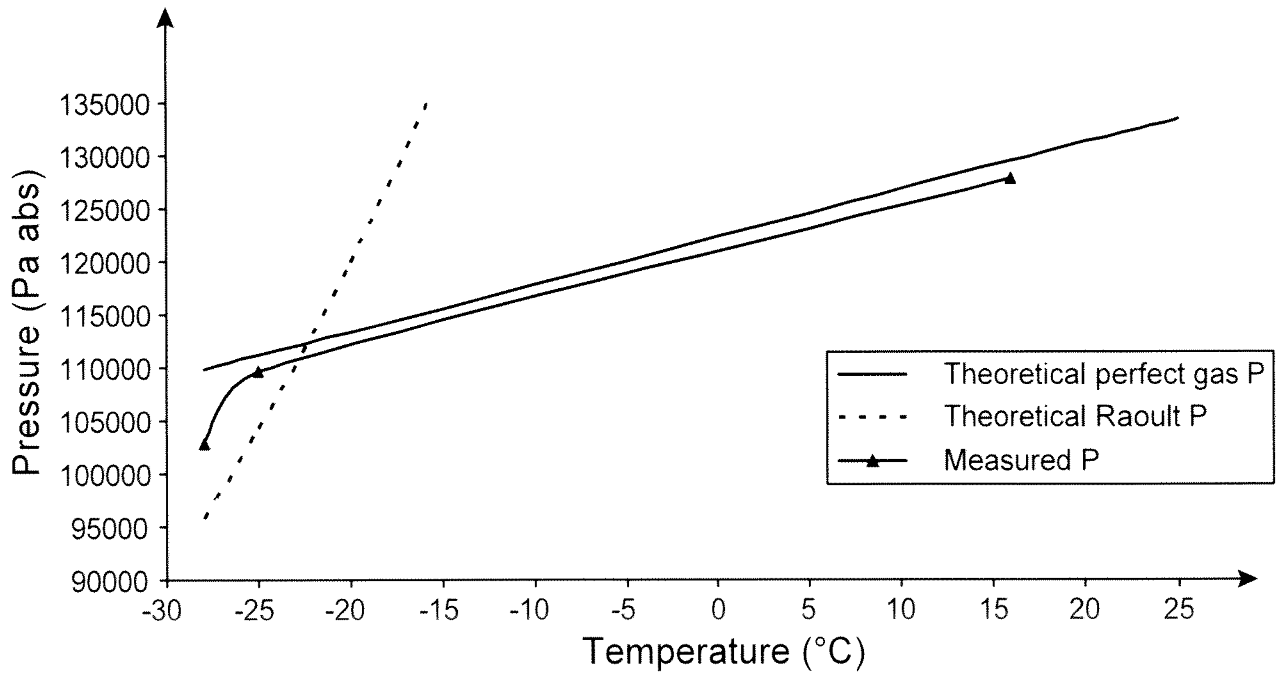
130000
125000
120000
115000
110000
105000
100000
95000
90000
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
Temperature (°C)
Theoretical perfect gas P
Theoretical Raoult P
Measured P

Fig.1A



Pressure (Pa abs)
135000
130000
125000
120000
115000
110000
105000
100000
95000
90000
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
Temperature (°C)
Theoretical perfect gas P
Theoretical Raoult P
Measured P

Fig.1B

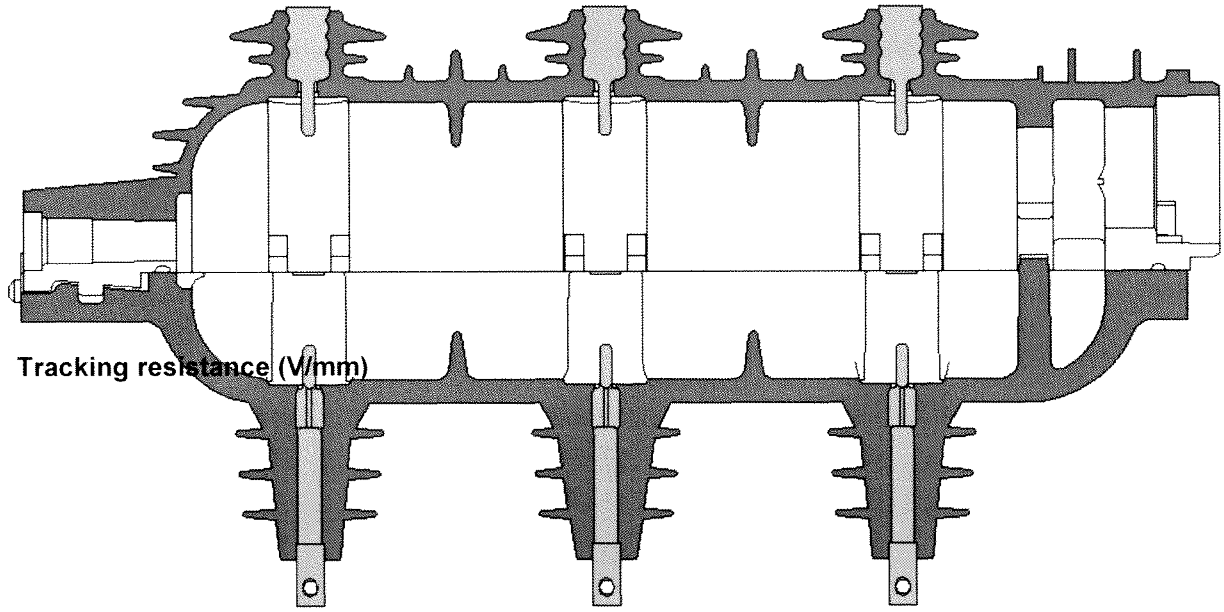

Tracking resistance (V/mm)

Fig.2A

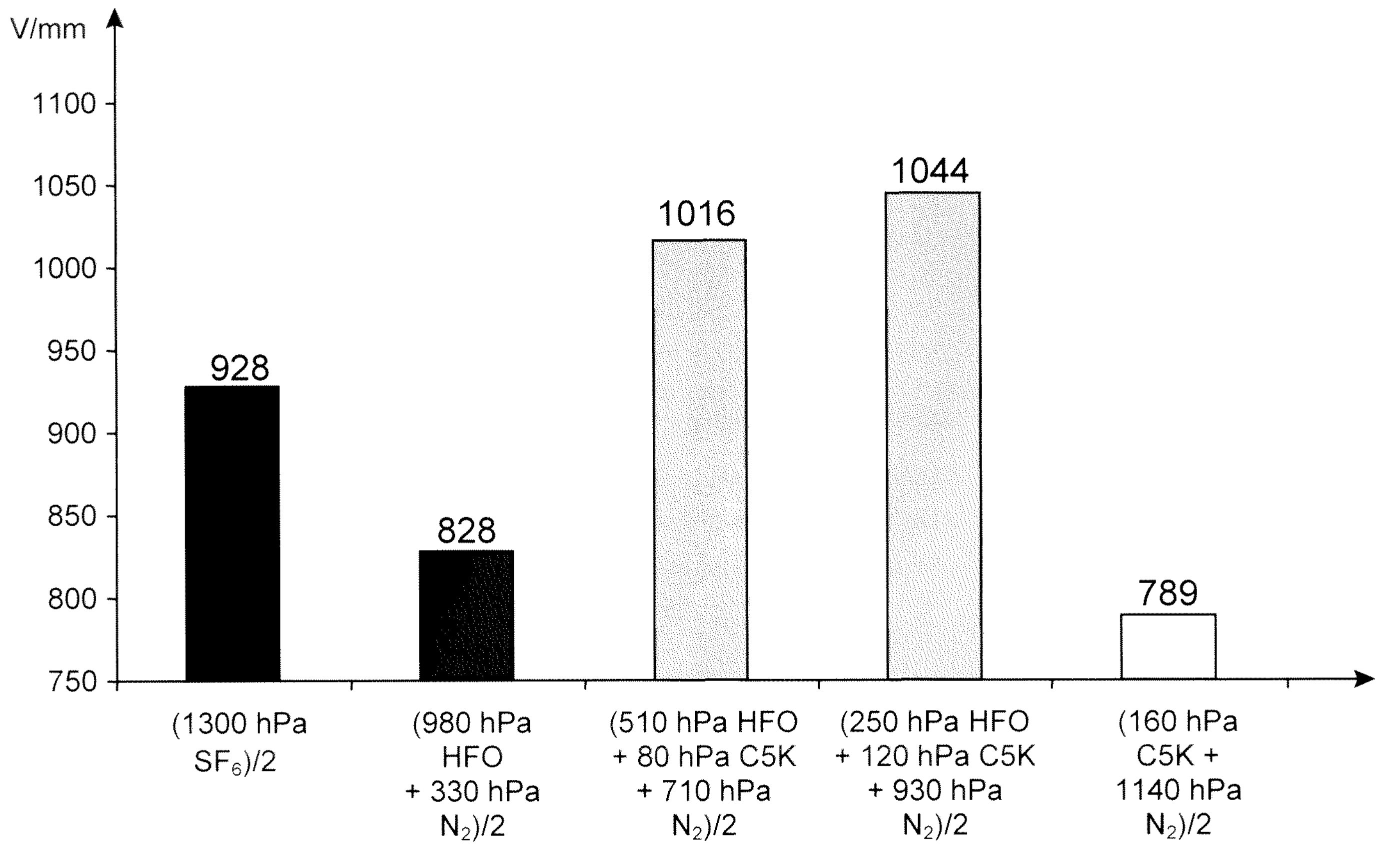

V/mm
1100
1050
1000
950
900
850
800
750
928
828
1016
1044
789
(1300 hPa SF6)/2
(980 hPa HFO + 330 hPa N2)/2
(510 hPa HFO + 80 hPa C5K + 710 hPa N2)/2
(250 hPa HFO + 120 hPa C5K + 930 hPa N2)/2
(160 hPa C5K + 1140 hPa N2)/2

Fig.2B

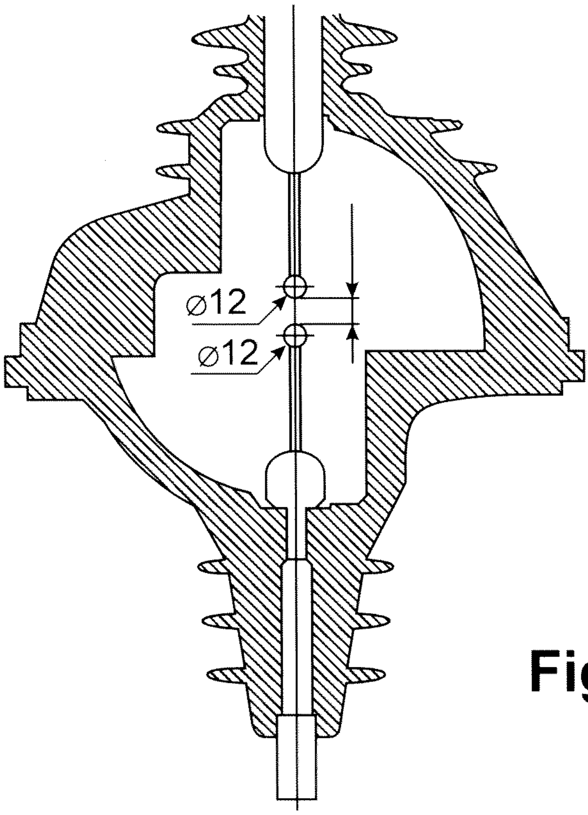

⌀12
⌀12

Fig.3A

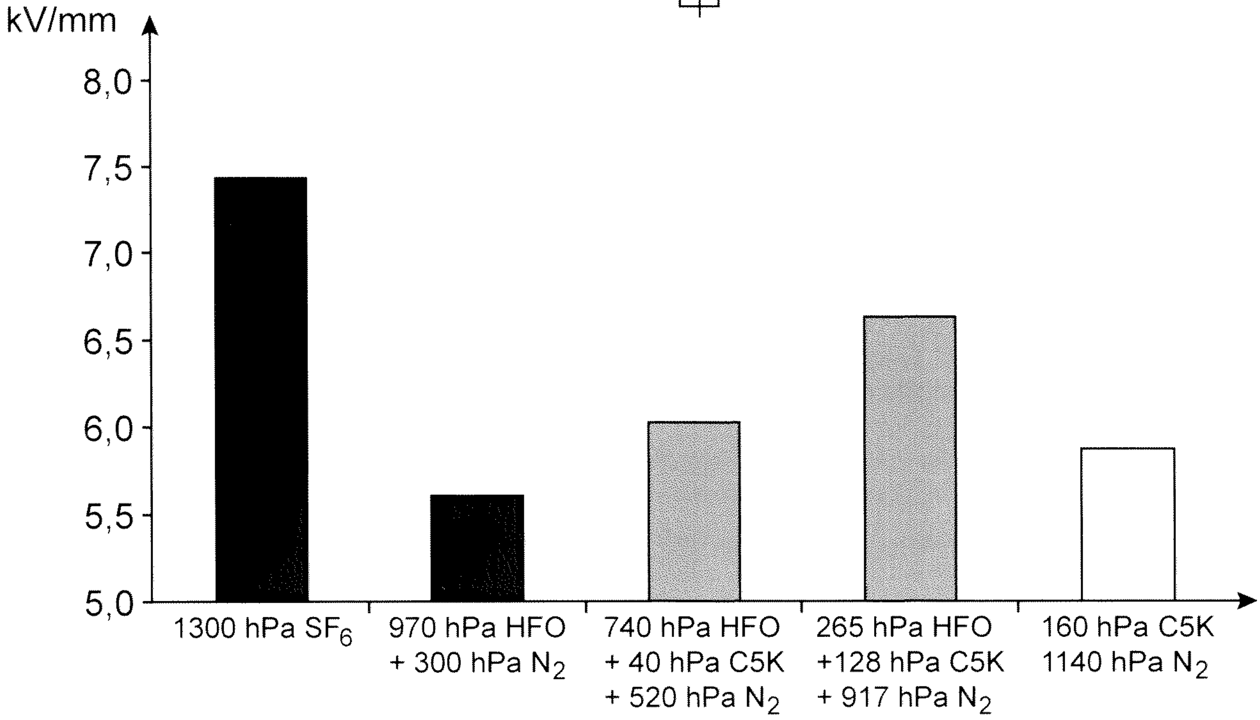

kV/mm
8,0
7,5
7,0
6,5
6,0
5,5
5,0
1300 hPa SF6
970 hPa HFO + 300 hPa N2
740 hPa HFO + 40 hPa C5K + 520 hPa N2
265 hPa HFO +128 hPa C5K + 917 hPa N2
160 hPa C5K 1140 hPa N2

Fig.3B

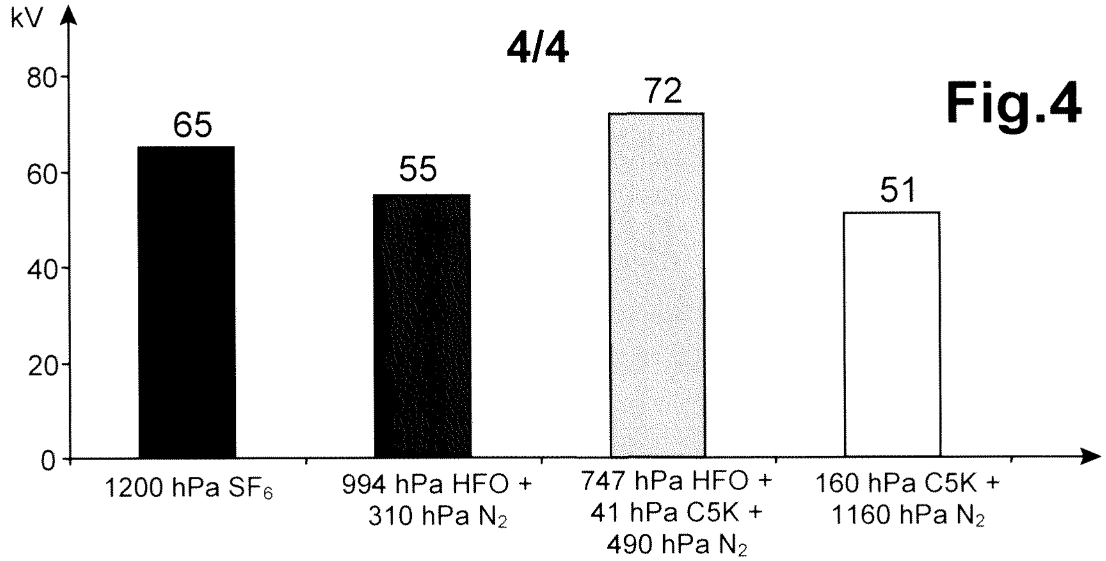


Fig.4

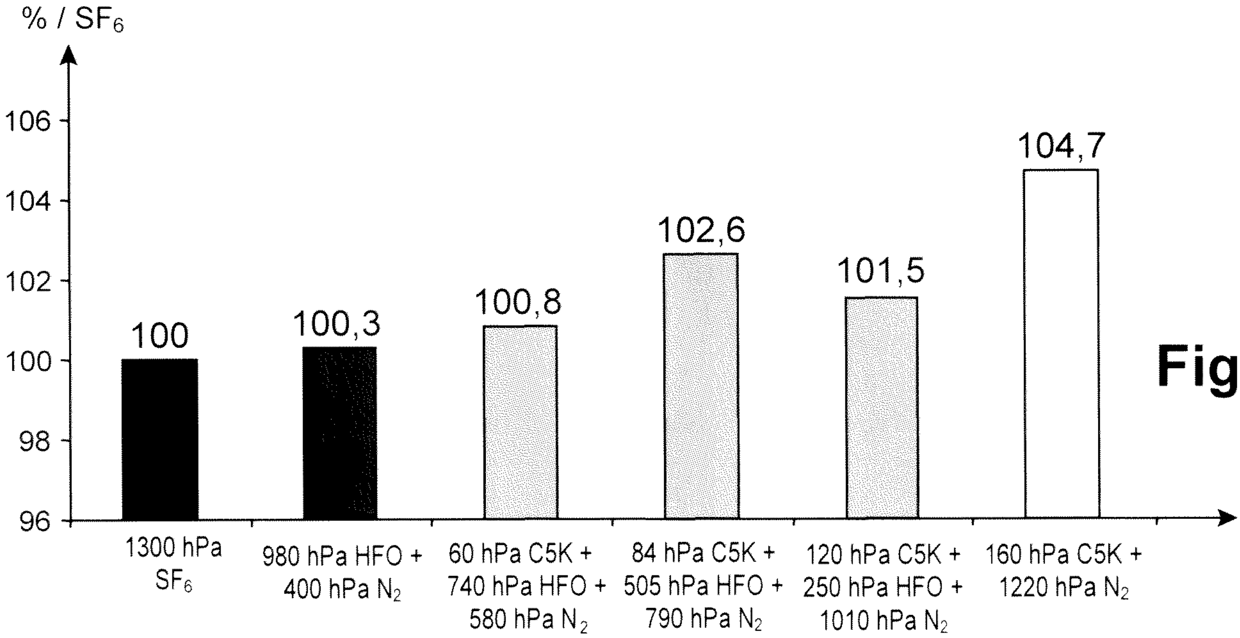


Fig.5

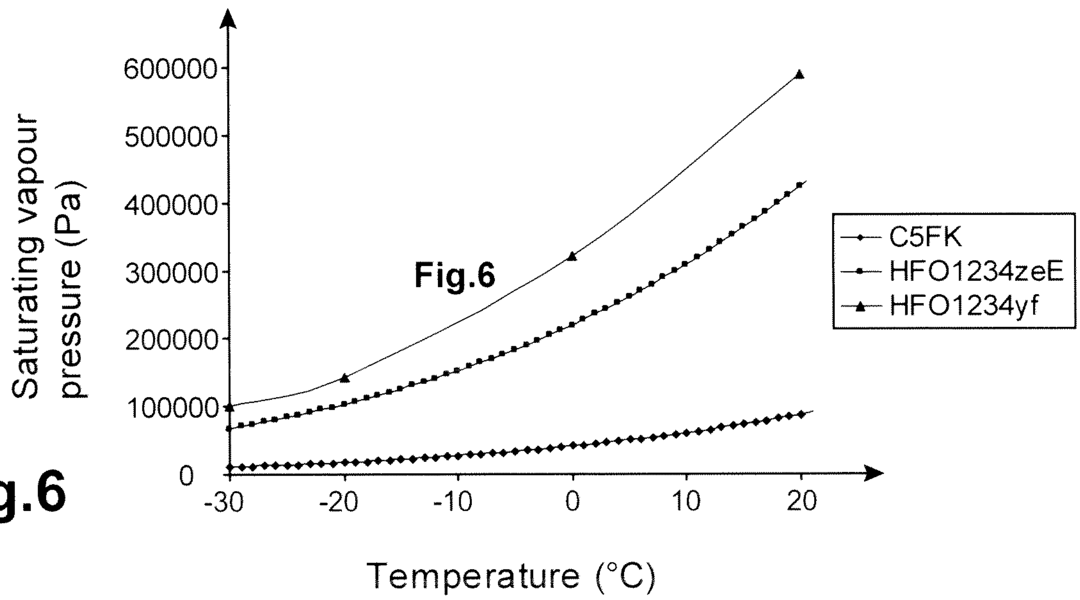


Fig.6