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(54) Benævnelse: **FILTRE DER OMFATTER OXYGEN-DEPLETEREDE SIC-MEMBRANER**

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FILTERS INCLUDING OXYGEN-DEPLETED SIC MEMBRANES

Description

The invention relates to the field of filtering structures made of an inorganic material intended for the filtration of liquids, in particular structures coated with a membrane in order to separate particles or molecules from a liquid, more particularly from water.

Filters that use ceramic or non-ceramic membranes for filtering various fluids, especially polluted waters, have long been known. These filters may operate according to the principle of frontal (dead-end) filtration, this technique involving passing the fluid to be treated through a filter media, perpendicularly to its surface. This technique is limited by the accumulation of particles and the formation of a cake on the surface of the filter media. This technique is therefore more particularly suitable for the filtration of liquids that are not heavily charged with pollutants (that is to say suspended liquid or solid particles).

According to another technique to which the present invention also relates, use is made of tangential (crossflow) filtration which, on the contrary, makes it possible to limit the accumulation of particles, owing to the longitudinal circulation of the fluid at the surface of the membrane. The particles remain in the circulating flow while the liquid can pass through the membrane under the effect of the pressure. This technique ensures stability of the performance and of the filtration level.

The strong points of tangential filtration are therefore its ease-of-use, its reliability owing to the use of organic and/or inorganic membranes whose porosity is suitable for carrying out said filtration, and its continuous operation. Tangential filtration requires little or no adjuvant and provides two separate fluids that may both be reusable: the concentrate (also referred to as retentate) and the filtrate (also referred to as permeate); it is considered a clean, environmentally friendly process. Tangential filtration techniques are especially used for microfiltration or ultrafiltration. The tangential configuration most often requires the use of at least two pumps, one of pressurization (or booster) and the other of recirculation. The recirculation pump often has the disadvantage of significant energy consumption.

Implementing filtering devices guaranteeing high flow rates of the filtrate would make it possible to limit energy consumption.

The present invention is therefore adapted both to tangential filters and to dead-end filtration filters.

Many structures of filters that operate according to the principles of tangential or dead-end filtration are thus known from the current art. They comprise or are constituted from tubular or parallelepiped supports made of a porous inorganic material that are formed of walls that delimit longitudinal channels parallel to the axis of said supports.

In the case of tangential filters, the filtrate passes through the walls then is discharged at the peripheral outer surface of the porous support. These filters are more particularly suitable for filtering liquids heavily charged with particles.

In the case of dead-end filters, the longitudinal channels are normally blocked at one end, for example alternately, so as to form inlet channels and outlet channels separated by the walls of the channels, the inlet and/or outlet channels being coated with the filter membrane through which all the liquid passes, the particles being retained by the membrane.

The surface of said channels is customarily covered with a membrane, preferably made of a porous inorganic material, referred to as a membrane, membrane layer, or separating membrane layer in the present description, the nature and the morphology of which are suitable for stopping the molecules or the particles having a size that is close to or greater than the median diameter of the pores of said membrane when the filtrate spills into the porosity of the porous support under the pressure of the fluid passing through the filter. The membrane is conventionally deposited on the internal surface of the channels by a process for coating the porous inorganic material with a slurry followed by a consolidating heat treatment, especially a drying and most commonly a sintering of the ceramic membranes.

Many publications indicate different configurations of the through-channels that aim to obtain a filter having the optimal properties for the application and in particular a highest exiting permeate flow and as homogeneous as possible from one channel to another in the section plane of the filter.

The work carried out by the applicant company has shown, according to another complementary approach, that within such filtering structures, it was useful to act on the chemical composition of the separating membrane, to further improve the filtration performance of the structure, or even the lifetime of the filter. Such an aim is in particular achieved by improving the abrasion resistance of the filter according to the invention, which can therefore operate effectively over a substantially greater lifetime.

Many documents of the art describe various possible compositions for the ceramic membrane made of porous inorganic material, without however establishing a causal relationship between the composition of the material constituting the membrane and the performance of the filter. According to one embodiment, application FR 2549736 proposes increasing the flow of liquid filtered by specifying the size of the particles forming the filtering layer relative to those forming the support. The alumina layers disclosed however have a flow considered to be small with regard to the present invention.

Other publications, for example patent application EP0219383A1, mention the use of silicon carbide and silicon nitride as the membrane material. According to example 2 of this publication, a filter body, the membrane layer of which is formed of SiC particles, is directly calcined in nitrogen at a temperature of 1050 °C. The abrasion resistance of the membrane thus obtained is, however, too low to allow filters having a long lifetime to be obtained.

Patent application WO03/024892 describes a method for preparing a support or a membrane produced from a mixture of large particles of alpha SiC, a metal silicon powder and a carbon precursor intended to form between the large grains a binder phase of fine beta SiC particles. The binder phase is finally converted according to this teaching into alpha SiC subsequently by firing at very high temperature (typically 1900 at 2300 °C).

The patent US 7,699.903 B2 describes separating membrane layers made of silicon carbide from a mixture of two powders of alpha SiC particles sintered together at a temperature between 1750 and 1950 °C.

Document EP2511250 describes a porous support comprising SiC grains, the surface of which is covered with a layer containing nitrogen. This layer of nitrogen is obtained by a nitriding treatment making it possible to control the resistivity for the decontamination of combustion gases. According to this publication, it is sought to obtain a filter or more specifically a nitrogen-doped SiC support element whose conductivity as a function of temperature is controlled. It is clearly indicated in this document that said nitriding is carried out on the SiC grains constituting the porous support. The document therefore describes the deposition of an additional layer (that is a separating membrane layer) on the internal surface of the channels or the external surface of the filter element before nitriding.

Patent application EP2484433 describes a particle filter for the purification of exhaust gases whose porous walls may comprise SiC and other particles than SiC, these particles being able to be chosen from an oxide, an oxynitride or a nitride of an element of groups 3 to 14 of the classification.

The object of the present invention is to provide a filter incorporating a resistant filter membrane whose filtration performance is substantially improved with respect to prior embodiments.

In particular, it was demonstrated by the work of the applicant company, described below, that it was possible to improve filtration performance, by a selection and appropriate treatment of the material constituting said membranes, said material being obtainable by the method according to the invention.

Most particularly, the work of the applicant company, described below, has demonstrated an advantage not yet described in the art to limit the oxygen content of the material constituting the membrane layers included in the filters when they consist essentially (or consist) of silicon carbide SiC. This treatment has made it possible, according to the present invention, to obtain membranes (also called separating membrane layers in the present description) whose filtration capacity was substantially improved.

In the present description, the terms separating membranes, separating layer or separating membrane layer are used interchangeably to designate such membranes allowing filtration.

The invention thus relates according to a first aspect to a filtering structure or filter configured to filter a liquid, and defined in claim 1. This filter comprising or composed of a support element made of a porous ceramic material, said element having a tubular or parallelepiped shape defined by an external surface and comprising in its inner portion a set of adjacent channels having axes parallel to one another and separated from one another by walls of said porous inorganic material, wherein at least some of said channels (and/or at least some of said external surface according to certain filter configurations) are covered on their internal surface with a porous separation membrane layer. During the operation of the filter, this layer, as indicated above, comes into contact with said fluid to be filtered circulating in said channels to allow the tangential or dead-end filtration thereof.

In a filter according to the present invention:

- said layer is made of a material essentially composed of sintered grains of silicon carbide (SiC), the SiC representing more than 97 % of the weight of the material constituting the separating membrane layer,

- the weight content of elemental oxygen of the layer is less than 0.5 %

- The porosity of the separating membrane layer is between 30 and 70 % and the median pore diameter is between 10 nanometers and 5 micrometers.

According to some preferred but non-limiting configurations of the filtering structure according to the invention:

- The SiC represents more than 99 % of the weight of the material constituting the separating membrane layer.

- The atomic concentration of oxygen measured by XPS at the surface of the SiC grains is less than 10 %, on the basis of the total amount of the Si, C and O elements.

- The carbon/oxygen ratio measured by XPS at the surface of the SiC grains is greater than 4.

- The porosity of the separating membrane layer is between 30 and 70 % and the median pore diameter is between 100 and 1500 nm and very preferably between 200 and 1000 nm, as can conventionally be measured by analysis of images obtained by scanning electron microscopy (SEM).

- The median size of the SiC grains in said material is between 20 nanometers and 10 micrometers, preferably between 0.1 and 1 micrometer.

- The weight content of elemental oxygen of the material constituting the separating membrane layer is less than or equal to 0.4 % and preferably is less than 0.3 %.

- The filter may further comprise one or more primer layers arranged between the material constituting the support element and the material constituting the separating membrane layer.

- The ratio 100 × ([D90-D10]/D50) of pore diameters is less than 10, preferably less than 5, the percentiles D10, D50 and D90 of a population of pores being the pore diameters corresponding respectively to the percentages of 10 %, 50 %, 90 % on the cumulative distribution curve of pore sizes classified by increasing order and measured by optical microscopy.

- The SiC constituting the grains is essentially in alpha crystallographic form.

In particular, the atomic concentration of oxygen, measured by XPS at the surface of the SiC grains in the separating membrane layer, is less than 10 %, on the basis of the total amount of the elements Si, C and O.

Finally, the invention relates to a method for manufacturing a separating membrane layer, in a tangential or dead-end filter, preferably tangential, defined in claim 11 and comprising the following steps:

- preparation of a slip from a powder of silicon carbide particles having a mean size of between 20 nanometers and 10 micrometers,

- application of said slip to the support element, under conditions that allow a thin layer of the slip to form on the internal portion of the channels of said filter,

- drying and then firing under an inert gas atmosphere at a temperature of between 1400 °C and 2000 °C and for a time sufficient to obtain a separating membrane layer on their internal surface of said channels essentially composed of sintered silicon carbide grains,

- treatment for removing some of the residual elemental oxygen present at the surface of said grains by the action of hydrofluoric acid.

As related to the porous support, the following indications are given regarding preferred but non-limiting embodiments of the present invention:

- The open porosity of the material constituting the support element is less than 70 %, in particular between 20 and 60 %.

- The median pore diameter of the material constituting the porous support is between 5 and 50 micrometers, more preferably between 10 and 40 micrometers.

- The porous support comprises and preferably consists of a ceramic material, preferably a non-oxide ceramic material, preferably selected from silicon carbide SiC, in particular liquid-phase or solid-phase sintered SiC, recrystallized SiC, silicon nitride, in particular Si_3N_4, silicon oxynitride, in particular Si_2ON_2, silicon aluminum oxynitride, or a combination thereof. Preferably, the support consists of silicon carbide, more preferably still of recrystallized SiC.

- The base of the tubular or parallelepiped shape is polygonal, preferably square or hexagonal, or circular. The tubular or parallelepiped shape has a longitudinal central axis of symmetry (A).

- In particular, in the case of a dead-end filter, the channels are blocked at one end, preferably alternately, in order to define inlet channels and outlet channels so as to force the liquid entering via the inlet channels on whose surface the membrane through which the liquid passes is deposited, before being discharged through the outlet channels.

- If the filter is tangential, the end of the tubular support can be in contact with a plate impermeable to the liquid to be filtered and perforated at the location of the channels facing it so as to form a filtering support placed in a tube or a filtration system. Another possibility may consist in introducing the tangential filter into the tube an impermeable peripheral seal at each end and around the filter so as to ensure the flow of permeate independently of the flow of concentrate.

- The elements have a hexagonal cross-section, the distance between two opposite sides of the hexagonal section being between 20 and 80 mm.

- The ducts of the filter elements are opened on their two ends.

- The ducts of the filter elements are alternately blocked on the feed face of the liquid to be filtered and on the opposite face.

- The ducts of the filter elements are open on the liquid introduction face and closed on the recovery face.

- A majority of the ducts, in particular more than 50 %, or even more than 80 %, are of square, round or oblong in cross-section, preferably round, and more preferably have a hydraulic diameter of between 0.5 mm and 10 mm, preferably between 1 mm and 5 mm. The hydraulic diameter Dh of a channel is calculated, in any transverse sectional plane P of the tubular structure, from the surface area of the cross section of the channel S of said channel and from its perimeter P, along said sectional plane and by applying the following conventional expression:

$$Dh = 4 \times S / P.$$

As indicated previously, the filter according to the invention may further comprise, besides the separating membrane layer, one or more primer layers arranged between the material constituting the support element and the material constituting the separating membrane layer. The role of this (these) primer layer(s) consists of facilitating the attachment of the separating layer and/or preventing the particles of the separating membrane from passing through the support, in particular during deposition by coating.

The following indications are also obtained:

The open porosity and the median pore diameter of the porous support described in the present description are determined in a known manner by mercury porosimetry.

The porosity and the median pore diameter of the separating membrane layer are advantageously determined according to the invention using a scanning electron microscope. For example, cross-sections of a wall of the support in transverse cross section are produced, as shown by the appended Figure 2, so as to visualize the entire thickness of the coating over a combined length of at least 1.5 cm. The images are acquired from a sample of at least 50 grains. The area and the equivalent diameter of each of the pores are obtained from images by conventional image analysis techniques, optionally after a binarization of the image that aims to increase the contrast thereof. A distribution of equivalent diameters is thus deduced, from which the median pore diameter is extracted. Similarly, it is possible to determine by this method a median size of the particles constituting the membrane layer.

One example of determining the median pore diameter or the median size of the particles constituting the membrane layer, by way of illustration, comprises the succession of the following steps, which are conventional in the domain:

- A series of SEM images is taken from the support with its membrane layer observed in a cross-section (that is to say throughout the thickness of a wall). For more clarity, the images are made on a polished section of the material. The image acquisition is carried out over a cumulative length of the membrane layer at least equal to 1.5 cm, in order to obtain values representative of the whole sample.

- The images are preferably subjected to binarization techniques, well known in image processing techniques, to increase the contrast of the contour of the particles or of the pores.

- For each particle or each pore constituting the membrane layer, a measurement of its area is carried out. An equivalent pore or grain diameter is determined, corresponding to the diameter of a perfect disc of the same area as that measured for said particle or for said pore (this operation possibly being carried out using dedicated software, in particular Visilog® sold by Noesis).

- a size distribution of particles or grains or diameter of pores is thus obtained according to a conventional distribution curve and a median size of the particles and/or a median pore diameter constituting the membrane layer are thus determined, this median size or this median diameter corresponding respectively to the equivalent diameter dividing said distribution into a first population including only particles or pores of equivalent diameter greater than or equal to that median size and a second population including only particles of equivalent diameter less than that median size or that median diameter.

For the purposes of the present description and unless otherwise mentioned, the median size of the particles the median diameter of the pores measured by microscopy respectively denotes the diameter of the particles or pores below which 50 % by number of the population is found. On the other hand, with regard to the diameter of pores measured on the substrate by mercury porosimetry, the median diameter corresponds to a threshold of 50 % of the population by volume.

The term “sintering” is used in a conventional manner in the field of ceramics (that is to say, in the sense indicated in international standard ISO 836:2001, point 120), a consolidation by heat treatment of a granular agglomerate. The heat treatment of the particles used as a starting charge to obtain the membrane layers according to the invention thus allows the junction and the development of their contact interfaces by movement of the atoms inside and between said particles.

The median diameter D_{50} of the particle powders used to produce the support or the membrane (the separating membrane layer) is conventionally given by a particle size distribution characterization, for example by means of a laser particle size analyzer.

The weight content of elemental oxygen of the separating membrane layer can be determined after melting under inert gas, for example by means of an analyzer sold under the reference TC-436 by the company LECO Corporation.

The atomic concentration of oxygen at the surface of the grains constituting the separating membrane layer is measured by X-ray photoelectron spectrometry, or XPS (also formerly called ESCA, for “electron spectroscopy for chemical analysis”). The sample is irradiated by monochromatic X-rays which cause the ionization of its atoms by photoelectric effect and an emission of electrons whose kinetic energy is characteristic of the elements and therefore of the chemical composition of the surface of the material analyzed over a depth of about 10 nanometers. The analysis depth is limited by the inelastic average free path of the electrons emitted in the material. The intensity of the lines of the photoelectron spectrum linked to the surface atomic concentration of elements decreases exponentially with the depth and according to the invention a relative concentration between elements is determined, that is to say for a membrane of SiC according to the invention, a concentration of elemental oxygen relative to the other elements essentially present Si and C.

The overall SiC content of the membrane (the separating membrane layer) can also be measured according to a protocol defined according to the standard ANSI B74.15-1992-(R2007) by difference between total carbon and free carbon, this difference corresponding to fixed carbon in the form of silicon carbide.

In the present description, unless otherwise specified, all the percentages are by weight.

A non-limiting example is given below, making it possible to produce a filter according to the invention, which of course is also not limiting on methods that make it possible to obtain such a filter and the method according to the present invention.

According to a first step, the filtering support is obtained by extruding a paste through a die configured according to the geometry of the structure to be produced according to the invention. The extrusion is followed by a drying and a firing in order to sinter the inorganic material constituting the support and to obtain the porosity and mechanical strength characteristics necessary for the application.

For example, when it is a question of an SiC support, it may in particular be obtained according to the following manufacturing steps:

- mixing a mixture including particles of silicon carbide of purity greater than 98 % and having a particle size such that 75 % by weight of the particles has a diameter of greater than 30 micrometers, the median diameter by weight of this particle size fraction (measured by laser particle size analyzer) being less than 300 micrometers. The mixture also includes an organic binder of the type derived from cellulose. Water is added and mixing is continued until a homogeneous paste is obtained, the plasticity of which allows extrusion, the die being configured for obtaining monoliths according to the invention.

- microwave drying of the raw monoliths for a sufficient time to bring the content of water that is not chemically bound to less than 1 % by weight.

- firing up to a temperature of at least 1300 °C in the case of a filtering support based on liquid-phase sintered SiC, silicon nitride, silicon oxynitride, silicon aluminum oxynitride or even BN and of at least 1900 °C and below 2400 °C in the case of a filtering support based on recrystallized or solid-phase sintered SiC. In the case of a nitride or oxynitride filtering support, the firing atmosphere is preferably a nitrogen-containing atmosphere. In the case of a recrystallized SiC filtering support, the firing atmosphere is preferably inert and more particularly argon. The temperature is typically maintained for at least 1 hour and preferably for at least 3 hours. The material obtained has an open porosity of 20 % to 60 % by volume and a median pore diameter of the order of 5 to 50 micrometers.

The filtering support is then coated according to the invention with a membrane (or membrane separation layer). One or more layers may be deposited in order to form a membrane according to various techniques known to the person skilled in the art: techniques for deposition using suspensions or slurries, chemical vapor deposition (CVD) techniques or thermal spraying, for example plasma spraying, techniques.

Preferably, the membrane layers are deposited by coating using slurries or suspensions. A first layer (called primer layer) is preferentially deposited in contact with the porous material constituting the substrate, acting as an attachment layer.

A non-limiting example of a primer mineral formulation includes 30 % to 50 % by weight of SiC powder(s) with a median diameter of 2 to 20 microns, the remainder being demineralized water (apart from any organic additives).

Typically, a primer formulation comprises from 25 to 35 % of a SiC powder with a median diameter of 7 to 20 microns, 15 to 25 % of an SiC powder with a median diameter of 2 to 6 microns, the remainder to 100 % being provided by demineralized water (apart from the organic additives or additions).

Although preferentially present, in certain filter configurations, this primer layer may be absent without departing from the scope of the invention.

A second layer of finer porosity is then deposited on the primer layer (or directly on the support), which constitutes the actual membrane or separating membrane layer. The porosity of the latter layer is adapted according to the techniques of the art, in particular by the temperature and the duration of the heat treatment of the layer described subsequently, to give the filter element its final filtration properties, in particular its selectivity by an adjusted value of its median pore diameter. A non-limiting example of a separating layer mineral formulation includes 30 % to 50 % by weight of SiC powder(s) with a median diameter of 0.1 to 1 microns, the remainder being demineralized water (apart from any organic additives).

In order to control the rheology of slurries and abide by a suitable viscosity (typically between 0.01 and 1.5 Pa.s, preferably 0.1 to 0.8 Pa.s under a shear gradient of $1s^{-1}$ measured at 22 °C according to the DINC 33-53019 standard), thickening agents (in proportions typically between 0.02 and 2 % of the weight of water). Binders (typically between 0.5 and 20 % of the weight of SiC powder), dispersing agents (between 0.01 and 1 % of the weight of SiC powder) can also be added. The thickeners preferably are cellulosic derivatives, the binders are preferably PVAs or acrylic derivatives and the dispersants preferably are of ammonium polymethacrylate type.

Organic additions expressed by weight of the slurry, in particular Dolapix A88 as deflocculant for example in a proportion of 0.01 % to 0.5 %, Tylose for example of MH4000P type as thickener in a proportion of 0.01 % to 1 %, PVA as bonding agent in an amount of 0.1 % to 2 % expressed by mass of solids, monoethylene glycol as plasticizer, and 95 vol% ethanol as surface tension reducer, are more particularly suitable.

These coating operations typically make it possible to obtain a primer layer having a thickness of about 30 to 40 micrometers after drying. During the second coating step, a membrane layer of thickness for example of about 30-40 µm is obtained after drying, this range of thickness being of course in no way limiting.

The specific steps of a method according to the invention for the deposition of the separating membrane layer according to the invention on the support, optionally above the primer layer described above, are described below:

According to a first preferred embodiment, a slip is prepared as indicated above from a powder or preferably several powders of silicon carbide particles of different particle sizes and in the presence of the quantity of water, preferably making it possible to observe the rheology and viscosity conditions described above, as well as in the presence of the organic agents required preferably so as to obtain a slip having a pH less than or equal to 9.

The slip is then applied to the support element, under conditions and by means adapted to allow the formation of a thin layer on the inner part of the channels of said filter, such as in particular described above.

After applying this layer, the support is then dried at ambient temperature typically for at least 10 minutes then heated to 60 °C for at least 12 hours. Finally, a porous separating membrane layer at the surface of the support channels is obtained by sintering in a furnace, in an atmosphere of a neutral gas such as argon, at atmospheric pressure (1 bar). The firing temperature is typically at least 1300 °C, preferably 1400 °C, preferably at least 1500 °C and is preferably less than 2000 °C, more preferentially less than 1900 °C, for a sufficient time, in particular of at least one hour, in order to obtain the required characteristics, in particular of porosity, of the membrane. The sintering temperature of the separating membrane layer is normally less than the sintering temperature of the support.

According to the invention, the filter comprising the filtering membrane layer is then subjected to an additional treatment aimed at modifying at least the surface state of the sintered SiC grains composing it, by eliminating some of the residual elemental oxygen present at the surface of said grains.

Any treatment known from the art making it possible to arrive at such a result can be used within the scope of the present invention. Mention may in particular be made of the following treatments:

- The filter support coated with its sintered membrane layer is immersed in a bath of hydrofluoric acid. Another acid fluoride, for example ammonium hydrogen fluoride, may also be suitable. With concentrations of 10 to 15 % by volume of HF, it is possible to carry out an effective treatment from 20 °C but it is preferable to carry out a treatment in the temperature range 60-90 °C. It is also possible to use an alkaline base, such as lithium hydroxide, sodium hydroxide or potassium hydroxide in a solution concentrated to at least 25 % by volume and at the boiling point of the base. In the case of a basic attack, washing is more complicated due to the risks of local hydrolysis of the alkali silicate solution within very fine pores. Advantageously, this treatment could be carried out on a membrane before being placed in service, or after cleaning or unclogging while in service. Indeed, the operation of the membrane by chemical route can be oxidizing, and a chemical treatment according to the invention may contribute to reducing the oxygen of the membrane.

- Before the acid treatment, the filter support coated with its sintered membrane layer may be subjected beforehand to a light oxidation step in air or a combustion gas, between 800 and 1400 °C, for 2 h before the washing makes it possible to eliminate any carbon residues present at the surface of the grains of the membrane after the recrystallization and before the oxygen elimination chemical treatment. Such a heat treatment also makes it possible to homogenize the silicate phase before treatment.

- The filter support filter coated with its sintered membrane layer is placed in a furnace at a firing temperature typically of at least 1000 °C, preferably between 1100 and 1400 °C, under a reducing atmosphere preferably comprising hydrogen gas (H_2). The heat treatment at this plateau is for example extended by 0.5 to 5 h, preferably 1 hour to 2 h. The treatment is for example carried out at atmospheric pressure (1 bar) or even below atmospheric pressure. The reducing atmosphere is preferably based on hydrogen, in particular a mixture H_2/N_2 or H_2/Argon preferably comprising at least 5 %, or even at least 10 % hydrogen by volume. The heat treatment may for example consist of one or more cycles comprising a rise in temperature of 5 °C/min up to the plateau temperature described above, heating at least 1 hour at said plateau temperature of 2 h and then falling down to room temperature with a ramp of 5 °C/min.

The thickness of the wet separating membrane layer obtained is preferably between 10 and 60 μm. The X-ray fluorescence and electron microscope analyses show that the material thus obtained consists essentially of alpha SiC grains bonded together by a binder phase where the silicon nitride is concentrated.

If the filter is configured for application in tangential filtration, it can be attached to a perforated plate at the location of the channel openings, in a sealed manner, in order to be installed in a tube or a filtration system. The heat treatment used to attach the perforated plate to the filter support must be carried out at a temperature below the decomposition temperature of the composite membrane.

If the filter has alternately blocked channels in order to obtain a membrane filter operating according to the principles of dead-end filtration and if the blockage is carried out after the deposition of the membrane at least for one face of the filter, either on the side of the inlet channels or on the outlet side, the blockage can be carried out with an SiC slip, the plugs being sintered at a temperature lower than the decomposition temperature of the composite membrane.

The figures associated with the following examples are provided in order to illustrate the invention and its advantages, without of course the embodiments thus described being able to be considered as limitations of the present invention.

In the appended figures:

- Figure 1 shows a conventional configuration of a tubular filter according to the current art, along a transverse sectional plane P.

- Figure 2 is a microscopy image of a filter showing the separating membrane layer within the meaning of the present invention.

Figure 1 shows a tangential filter 1 using the current technique and according to the present invention, as used for filtering a fluid such as a liquid. Figure 1 shows a schematic view of the transverse sectional plane P. The filter comprises, or most often consists of, a support element 1 made of a porous, preferably non-oxide, inorganic material. The element conventionally has a tubular shape with a central longitudinal axis A, delimited by an external surface 2. It comprises in its inner portion 3 a set of adjacent channels 4, having axes that are parallel to one another and separated from one another by walls 8. The walls are made of a porous inorganic material that lets the filtrate pass from the inner portion 3 to the outer surface 2. The channels 4 are covered over their internal surface with a separating membrane layer 5 deposited on an attachment primer, as shown by the electron microscopy image shown in Figure 2. This separating membrane layer 5 (or membrane) comes into contact with said fluid circulating in said channels and allows filtration thereof.

In Figure 2, an electron microscopy photograph taken on a channel 4 of Figure 1 is shown. Observed in this figure are the porous support 100 of high porosity, the primer layer 102 that enables the adhesion of the membrane separation layer 103 of finer porosity.

According to another configuration not shown of another filter according to the invention, that filter is configured so that the fluid to be treated initially passes through the external wall, the permeate being collected this time at the outlet of the channels. According to such a configuration, the filtering membrane layer is advantageously deposited on the external surface of the filter and covers at least a part thereof.

The following examples are provided solely by way of illustration. They are not limiting and make it possible to better understand the technical advantages related to the implementation of the present invention:

The supports according to all the examples are obtained according to the same experimental protocol below:

Mixed in a mixer are:

- 3000 g of a mixture of the two powders of silicon carbide particles with a purity of greater than 98 % in the following proportions: 75 % by weight of a first powder of particles having a median diameter of the order of 60 micrometers and 25 % by weight of a second powder of particles having a median diameter of the order of 2 micrometers. (For the purposes of the present description, the median diameter d_{50} denotes the diameter of the particles below which 50 % by weight of the population of said particles is found).

- 300 g of an organic binder of the type derived from cellulose.

Water is added in an amount of about 20 % by weight relative to the total weight of SiC and of organic additive and mixing is continued until a homogeneous paste is obtained, the plasticity of which allows the extrusion of a structure of tubular shape, the die being configured for obtaining monolith blocks the channels and the outer walls of which have a structure according to the desired configuration and as represented in appended Figures 1 to 2. Thus, for each configuration, 5 to 10 green supports having a diameter of 25 mm and a length of 30 cm are synthesized.

More precisely, the fired monoliths have round channels with a hydraulic diameter of 2 mm, the peripheral half-moon channels shown in the figures having a hydraulic diameter of 1.25 mm. The average thickness of the outer wall is 1.1 mm and the OFA (Open Front Area) of the inlet face of the filter is 37 %. The OFA (open front area) is obtained by calculating the ratio, as a percentage, of the area covered by the sum of the transverse cross sections of the channels to the total area of the corresponding transverse cross section of the porous support.

The green monoliths thus obtained are dried using a microwave system for a sufficient time to bring the content of water that is not chemically bound to less than 1 % by mass.

The monoliths are then fired up to a temperature of at least 2100 °C which is maintained for 5 hours. The material obtained has an open porosity of 43 % and a mean pore distribution diameter of the order of 25 micrometers, as measured by mercury porosimetry.

<u>Example 1 (comparative):</u>

According to this example, a silicon carbide separating membrane layer is then deposited on the inner wall of the channels of a support structure as obtained previously, according to the method described below:

A primer for attaching the separating layer is firstly constituted by a slip whose mineral formulation includes 30 % by weight of a powder of black SiC grains (SIKA DPF-C) whose median diameter D50 is about 11 micrometers, 20 % by weight of a powder of black SiC grains (SIKA FCP-07), the median diameter D50 of which is approximately 2.5 micrometers, and 50 % of deionized water.

A slurry of the material constituting the membrane filtration layer is also prepared, the formulation of which includes 50 % by weight of SiC grains (d_{50} of about 0.6 micrometer) and 50 % demineralized water.

The rheology of the slurries was adjusted by adding organic additives to 0.5-0.7 Pa.s under a shear gradient of 1 s^{-1}, measured at 22 °C according to the DINC 33-53019 standard.

These two layers are deposited successively according to the same process described below: the slurry is introduced into a stirred tank (20 rpm). After a deaeration phase under a slight vacuum (typically 25 millibar) while maintaining the stirring, the tank is placed under a positive pressure of about 0.7 bar in order to be able to coat the inside of the support from its bottom portion up to its upper end. This operation takes only a few seconds for a 30 cm long support. Immediately after coating the slurry onto the inner wall of the channels of the support, the excess is discharged by gravity.

The supports are thus dried at ambient temperature for 10 minutes then at 60 °C for 12 h. The supports thus dried are then fired in Argon at a temperature of 1400 °C for 2 h at ambient pressure.

A transverse cut is made through the filters thus obtained. The structure of the membrane is observed with a scanning microscope.

<u>Example 2 (according to the invention):</u>

According to this example, the procedure is identical to example 1, but the filter obtained is subjected to an additional treatment by immersion in a concentrated solution of hydrofluoric acid (20 % volume), followed by successive rinses to bring its pH to 6.

Example 3 (comparative):

According to this example, the procedure is identical to example 1, but the filter obtained is additionally subjected to an oxidation treatment in steam at 350 °C for 8 hours.

The properties and the characteristics of the filters thus obtained are measured as follows:

On the basis of electron microscopy images, the average thickness of the successive layers obtained for each example is measured by image analysis.

The average thickness of the separating layer is of the order of 45 microns for all the examples. The median pore diameter of the separating membrane layer is approximately 250 nm for all the examples.

The other results as measured as indicated above are reported in table 1 which follows.

The details of the flow measurement (relative water flow rate) carried out:

At a temperature of 25 °C a fluid consisting of demineralized water feeds the filters to be evaluated under a transmembrane pressure of 0.5 bar and a circulation rate in the channels of 2 m/s. The permeate (water) is recovered at the periphery of the filter. The characteristic flow rate measurement of the filter is expressed in L/min per filtration surface area after 20 h of filtration. In the table, the flow rate results have been expressed with reference to the data recorded for comparative example 1. More specifically, a value of greater than 100 % indicates an increased flow rate with respect to the reference (example 1) and therefore an improvement in the filtration capacity.

The characteristics and properties of the filters obtained according to examples 1 to 3 are given in table 1 below.

Table 1

	Reference example 1	t equal 2 according to the invention	Comparative example 3
Additional processing	none	HF Immersion	Water vapor oxidation
SiC weight content of the membrane (%) *	99.0	99.3	98.8
Elemental oxygen weight content of the membrane (%) **	0.50	0.24	0.81
Membrane surface atomic percentage ***			
Si	40.5	42.2	42.2
C	44.2	49.0	37.6
O	15.3	8.8	20.2
C/O ratio***	2.9	5.6	1.9
Average thickness of the membrane (micrometers)	45	45	45
Median pore diameter of the membrane (nanometers)	250	250	250
Relative flow measurement	100	138	61
* Measured according to standard ANSI B74.15-1992- (R2007) ** Measured by LECO *** Measured by XPS			

The results grouped together in table 1 above indicate that example 2 according to the invention has a filtration capacity much greater than that of the reference filter (example 1).

The analysis of the data reported in the preceding table makes it possible to directly correlate this higher capacity with the residual oxygen content in the membrane layer.

Lastly, the results grouped together in the table also indicate that the material used according to the invention for manufacturing the separating membrane layer (membrane in table 1) can only be obtained according to certain method conditions not yet described in the prior art, aimed at very greatly limiting the oxygen content present therein and more particularly on the surface of the SiC grains constituting the membrane.

PATENTKRAV

1. Filter til filtrering af en væske, som omfatter eller er sammensat af et støtteelement (1), der er fremstillet af et porøst keramisk materiale, hvilket element har en rørformet eller parallelepipidumformet facon, der er defineret ved en udvendig overflade (2), og i dets indvendige del (3) omfatter et sæt tilstødende kanaler (4) med akser, der er parallelle med hinanden og adskilt fra hinanden af vægge (8) af det porøse uorganiske materiale, hvor:

- mindst nogle af kanalerne (4) er dækket på deres indvendige overflade med et porøst adskillende membranlag (5), og/eller

- mindst en del af den udvendige overflade (2) er dækket med et porøst adskillende membranlag (5);

hvilket filter er **kendetegnet ved, at**:

- laget er fremstillet af et materiale, der i alt væsentligt er sammensat af sintrede korn af siliciumcarbid (SiC), idet SiC repræsenterer mere end 97 % af vægten af det materiale, der udgør laget,

- vægtindholdet af oxygen-grundstof i det adskillende membranlag, bestemt ved inert gasfusion, er 0,5 %,

- porøsiteten og medianporediameteren af det adskillende membranlag, målt ved analyse af negativer opnået med scanningelektronmikroskop, er henholdsvis mellem 30 og 70 % og mellem 10 nanometer og 5 mikrometer.

2. Filter ifølge det foregående krav, hvor SiC repræsenterer mere end 99 % af vægten af det materiale, der udgør det adskillende membranlag.

3. Filter ifølge et af de foregående krav, hvor atomkoncentrationen af oxygen målt ved XPS ved SiC-kornenes overflade er mindre end 10 %, på grundlag af den samlede mængde af Si-, C- og O-grundstofferne.

4. Filter ifølge et hvilket som helst af de foregående krav, hvor carbon/oxygen-forholdet målt ved XPS ved SiC-kornenes overflade er større end 4.

5. Filter ifølge det foregående krav, hvor mediansstørrelsen af SiC-kornene i materialet er mellem 20 nanometer og 10 mikrometer.

6. Filter ifølge et hvilket som helst af de foregående krav, hvor det adskillende membranlags tykkelse er mellem 10 og 60 mikrometer.

7. . Filter ifølge et hvilket som helst af de foregående krav, hvor vægtindholdet af oxygen-grundstof i det materiale, der udgør det adskillende membranlag, er mindre end eller lig med 0,4 % og fortrinsvis er mindre end 0,3 %.

8. Filter ifølge et hvilket som helst af de foregående krav, hvor det porøse støtteelement omfatter eller er sammensat af et materiale, der er valgt ud af siliciumcarbid, SiC, især sintret væskefase- eller fastfase-SiC, omkrystalliseret SiC, siliciumnitrid, især Si_3N_4, siliciumoxynitrid, især Si_2ON_2, siliciumaluminiumoxynitrid eller en kombination deraf.

9. Filter ifølge et hvilket som helst af de foregående krav, hvor den åbne porøsitet af det materiale, der udgør støtteelementet, er mellem 20 % og 60 %, idet medianporediameteren af det materiale, der udgør den porøse støtte, fortrinsvis er mellem 5 og 50 mikrometer.

10. Filter ifølge et hvilket som helst af de foregående krav, der endvidere omfatter et eller flere primerlag, der er indrettet mellem det materiale, der udgør støtteelementet, og det materiale, der udgør det adskillende membranlag.

11. Fremgangsmåde til fremstilling af et adskillende membranlag, i et tangential- eller frontalfilter, ifølge et hvilket som helst af kravene 1 til 10, fortrinsvis et tangentialfilter, der omfatter følgende trin:

- fremstilling af en opslæmning af et pulver af siliciumcarbidpartikler med en middelstørrelse på mellem 20 nanometer og 10 mikrometer,

- påføring af opslæmningen på støtteelementet under forhold, der åbner mulighed for dannelse af et tyndt lag af opslæmningen på den indvendige del af filterets kanaler,

- tørring og derefter fyring under en inert gasatmosfære ved en temperatur på mellem 1400 °C og 2000 °C og i et tidsrum, der er tilstrækkeligt til at opnå et adskillende membranlag på de indvendige overflader af kanalerne, der i alt væsentligt er sammensat af sintrede siliciumcarbidkorn,

- behandling for at fjerne noget af det resterende oxygen-grundstof, der er til stede ved overfladen af kornene, ved virkningen af flussyre.

12. Anvendelse af et filter ifølge et hvilket som helst af kravene 1 til 10 til filtrering af væsker, især af en vandig væske.

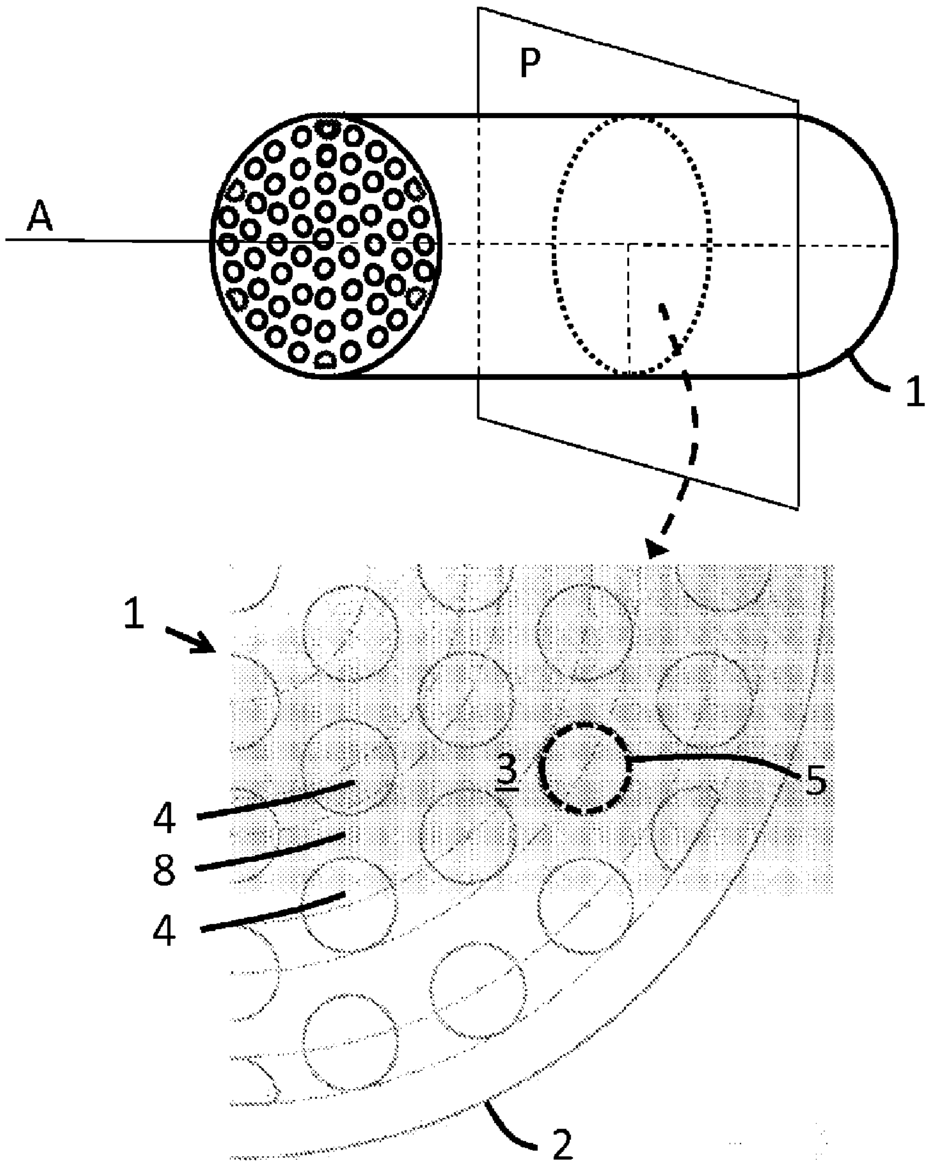

FIG. 1

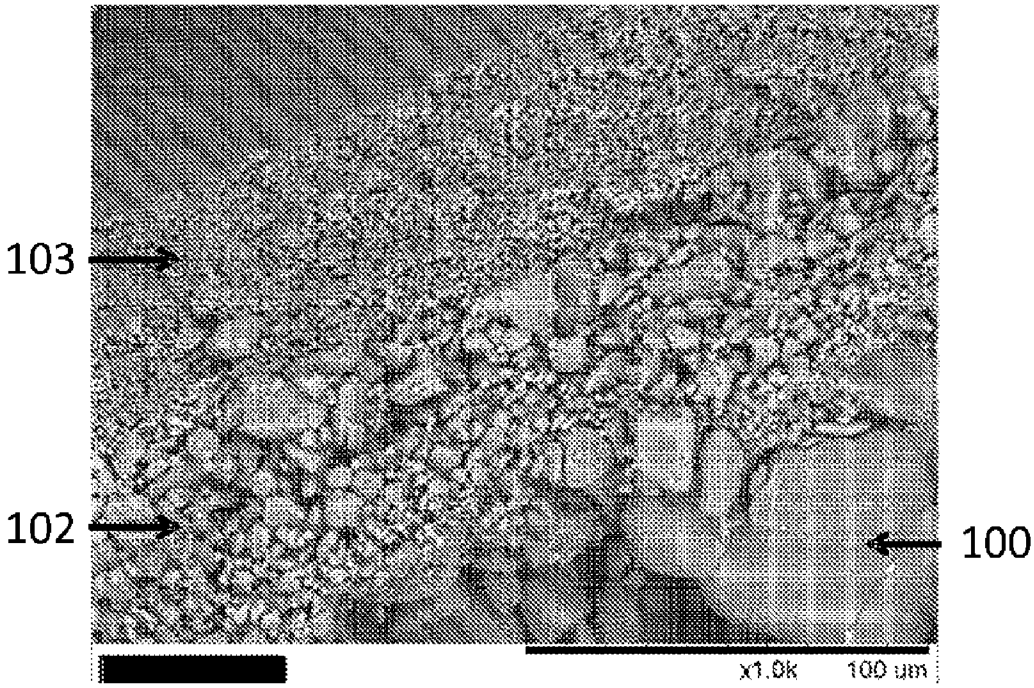

FIG. 2