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(54) **STOPPER FOR SEALING BOTTLES, PARTICULARLY FOR SEALING BOTTLES OF WINE FOR AGEING**

STOPFEN ZUR ABDICHTUNG VON FLASCHEN, INSBESONDERE ZUR ABDICHTUNG VON WEINFLASCHEN ZUM ZWECK VON DEREN ALTERUNG

BOUCHON PERMETTANT DE BOUCHER HERMÉTIQUEMENT DES BOUTEILLES, EN PARTICULIER DES BOUTEILLES DE VIN QU'IL FAUT LAISSER VIEILLIR

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DescriptionTechnical field

5 **[0001]** The present invention relates to a stopper for sealing bottles, particularly for sealing bottles of wine for ageing, the stopper having the characteristics stated in the preamble of the principal claim.

Technological background

10 **[0002]** In the technical field of bottling drinks, particularly wine, there is a known need to replace the conventional cork stoppers with synthetic stoppers made from polymer material. This need arises from specific economic factors, significant technical drawbacks associated with conventional stoppers, including the possibility that cork stoppers will release substances which can alter the flavour of the wine, and the ease with which bacteria and moulds can develop on the wine.

15 **[0003]** To provide a positive response to this need, stoppers made from polymer material, usually expanded, have been developed, but these stoppers do not allow a controlled oxygen exchange between the inside and the outside of the bottle, and therefore they prevent a correct wine maturing process, while causing the well-known problems of oxidation or reduction of the wine in the bottle. This limitation is particularly serious for wines for ageing, usually red vintage wines, which require long maturing periods to obtain the flavour properties which characterize them.

20 **[0004]** In an attempt to resolve this problem, a synthetic stopper has been developed which includes a passage for putting the inside of the bottle in communication with the outside, sealed by a membrane intended to selectively regulate the flow of oxygen through the passage, between the inside and the outside of the bottle.

[0005] An example of this prior art is described in international patent application WO 02/055397, in which this membrane is inserted into a support sleeve inserted into the passage formed in the stopper, or also from EP0629559.

25 **[0006]** However, the results achieved with the stoppers described therein are not completely satisfactory in respect of the maturing of wines and consequent oxidation or reduction phenomena of the wine in the bottle.

Description of the invention

30 **[0007]** The problem tackled by the present invention is that of providing a stopper for sealing bottles, which is structurally and functionally designed to overcome the limitations described above with reference to the cited prior art.

[0008] This problem is resolved by the invention by means of a stopper produced in accordance with the claims below.

Brief description of the drawings

35 **[0009]** The characteristics and advantages of the invention will be made clearer by the detailed description of some preferred examples of embodiment thereof, illustrated, for the purposes of guidance and without restrictive intent, with reference to the attached drawings, in which:

- 40 - Figure 1 is a schematic view, in longitudinal section, of a first example of a stopper made according to the present invention,
- Figure 2 is a schematic view in longitudinal section and on an enlarged scale of a detail of the stopper of Figure 1,
- Figure 3. is a schematic view in longitudinal section of a second example of a stopper made according to the present invention,
- 45 - Figure 4 is a schematic view in longitudinal section of a third example of a stopper made according to the present invention.

Preferred embodiments of the invention

50 **[0010]** In Figures 1 and 2, the number 1 indicates the whole of a first example of a stopper, made according to the present invention, intended for sealing bottles of wine, particularly wine for ageing which requires a considerable period of maturing.

[0011] The stopper 1 comprises a main body 2, of generally cylindrical shape with rounded edges and having dimensions such as to allow it to be housed and engaged in an aperture 3a of a bottle 3 only partially indicated by broken lines in Figure 1.

55 **[0012]** The main body 2 is made from any polymer material having mechanical and sealing characteristics such that it is as impermeable as possible to liquids, gases and vapours such as expanded polyethylene, or polyolefin and styrene based copolymers, or elastomers in general.

[0013] A passage 4 is formed in the main body 2 and extends along a longitudinal axis X of the body 2, opening at its

opposite ends which form a first surface 5 and a second surface 6. When the stopper 1 is inserted into the bottle 3, the first and second surfaces 5 and 6 are intended to face the outside environment in one case, and the inside of the bottle in the other case, thus forming an outer surface and an inner surface of the stopper 1. Clearly, the stopper is of a two-way type; that is to say it can be inserted into the neck of the bottle in either of the two possible directions, so that the outer surface can be formed by the first surface 5 or by the second surface 6.

[0014] A permeable element is inserted into the passage 4, to provide adequate regulation of the passage of oxygen between the inside and the outside of the bottle. This permeable element can be of the membrane type, as described in detail below with reference to Figures 1 and 2, or can be of the insert type, that is to say a rod-like cylindrical body, extending predominantly along the axis of the passage 4, as described below.

[0015] In the first preferred example described here, the passage 4 comprises a first cylindrical portion of reduced diameter 7, extending from the second surface 6 towards a median portion 8 of the passage 4, and a second portion 9, also cylindrical but having a larger diameter, extending from the median portion 8 towards the first surface 5.

[0016] The median portion 8 is delimited towards the second portion 9 by a circular bead 10 extending radially towards the inside of the passage 4, and it is delimited towards the first portion 7 by a shoulder 11.

[0017] The median portion 8 has surfaces slightly inclined with respect to the axis X from the bead 10 to the shoulder 11, and forms a seat for housing a support sleeve 12 whose shape is substantially conjugate with that of the median portion 8. The sleeve 12, shown in greater detail in Figure 2, thus has a generally truncated conical shape with a profile tapered along the axis X from its major base 13 to its minor base 14.

[0018] In the seat 8, the sleeve 12 is positioned with its minor base bearing on the shoulder 11 and with its major base 13 next to the bead 10.

[0019] A through hole 15, intercepted in its central area by a membrane 16 which extends transversely with respect to the axis X and is fixed to the support sleeve 12 by particular welding or moulding methods, is formed along the longitudinal axis of the sleeve 12, coinciding with the axis X.

[0020] The membrane 16 therefore intercepts the hole 15 and consequently the entire passage 4 for communication between the first and second surfaces 5 and 6 of the stopper 1. The characteristics of the membrane 16, described in detail below, are such as to efficiently regulate the passage of gases and vapours, particularly oxygen, through the passage 4.

[0021] In the specific case detailed here, the diameter of the hole 15 is equal to that of the first portion 7, so as to form an extension thereof, but clearly it is possible for it to have a different diameter. The hole 15 can also have different cross sections in the portions separated by the membrane 16. A projection 19, extending radially towards the walls of the seat 8 from the edge of the major base 13, is also conveniently provided around the outer shell of the sleeve 12.

[0022] The projection 19 preferably has a sharp edge, so that it can be more easily inserted into the walls of the seat 8.

[0023] The production of the stopper 1 comprises a first step of producing the main body 2 of the suitable polymer material, with the provision of the passage 4. This step can be carried out by injection moulding, extrusion, or any other method suitable for the purpose.

[0024] The support sleeve 12 is made separately, for example by injection moulding of polypropylene, polyamide or ABS, and the membrane 16 is fixed therein.

[0025] The membrane 16 can be fixed to the sleeve 12 in the most suitable way. For example; in the embodiment described here, the membrane is positioned on a shoulder 17 formed in the hole 15 and retained in position by a tubular insert 18 bearing on the shoulder 17 and subsequently heat-welded. To improve the retention of the membrane, it is possible to create pointed formations (not shown in the figures) on the shoulder 17 and/or on the tubular insert 18, projecting towards the membrane 16, with a pressure retaining system of the flange type.

[0026] Similarly, the membrane 16 can be fixed to the sleeve 12 by overmoulding the plastics material forming the sleeve on to the membrane which has previously been positioned in the mould, or by ultrasonic welding. In particular, the overmoulding method is particularly preferred if the polymer material forming the sleeve 12 and that forming the membrane 16 are chemically compatible with each other.

[0027] The sleeve 12 is then inserted mechanically into the passage 4 of the main body 2, until the minor base 14 bears on the shoulder 11, thus defining its correct position in the seat 8.

[0028] It should be noted that the step of inserting the sleeve 12 is facilitated by its truncated conical shape and that the provision of the bead 10 prevents its movement out of the main body 2. When the stopper 1 is inserted and engaged in the aperture 3a of the bottle 3, the main body is normally subjected to radial compression which ensures that the stopper is retained in the sealing position, and that there is sufficient resistance to the passage of gases and liquids between the stopper and bottle. Following this compression, the projection 19 is pressed forcefully against the walls of the seat 8, thus forming a means of preventing the passage of gases or liquids between the sleeve 12 and the main body 2, and an efficient means of fixing the sleeve 12 inside the seat 8.

[0029] The membrane 16 is impermeable to liquids, and thus does not allow the passage of any liquids through it.

[0030] The membrane 16 is also made from polymer material having characteristics such that it allows a sufficient flow of oxygen for the process of maturing the wine contained in the bottle, this flow being measured at approximately

0.1 - 5 milligrammes (mg) per month, depending on the type of wine. In particular, for most of the wines concerned, the monthly flow of oxygen which must pass from the outside to the inside of the bottle for the wine to mature correctly is in the range from 0.2 to 2 mg.

[0031] If suitable allowance is made for a minimum constant quantity of oxygen which inevitably passes between the stopper and the neck of the bottle, and if the same differential partial pressure of oxygen is assumed to exist between the two sides of the membrane, this flow depends substantially on the area of the membrane exposed to the flow, on its thickness and on its permeability to oxygen.

[0032] The area of the membrane 16 exposed to the flow of oxygen is identical, in the case described here, to the area of the cross section of the hole 15, whose diameter varies from approximately 0.1 to 10 mm, preferably from 1 mm to 7 mm. The area concerned is therefore in the range from 0.0078 to 78.5 mm², preferably from 0.7 to 38.5 mm².

[0033] On the other hand, the thickness of the membrane 16 is in the range from 5 to 2000 microns, preferably from 10 to 1000 microns. If the membrane has a thickness of less than about 100 microns, it is preferably placed on a supporting material, for example a suitably treated paper-based material, whose characteristics must be such as not to affect the permeability of the membrane.

[0034] Additionally, in the case of membranes of a certain thickness, the membrane 16 can be moulded in one piece with the sleeve 12, thus forming a monolithic permeable element made from a single material.

[0035] It should be noted that, in the preferred case described here, there is only one membrane. However, it is possible to control the flow of oxygen by providing more than one membrane. In this case, it must be possible to provide an equivalent total area and an equivalent total thickness, defined as the surface and thickness of a hypothetical membrane which by itself would offer the same resistance to the flow of oxygen as the plurality of membranes provided in the stopper.

[0036] The determination of this equivalent total area and thickness will clearly depend on the way in which the membranes are positioned in the stopper, for example on whether they are positioned in series in the same passage or in parallel in different passages.

[0037] The oxygen permeability of the membrane 16 at ambient temperature, fixed at 20°C, is in the range from 10⁻⁷ to 10⁻¹¹ (Ncm³*cm/cm²*cm_{Hg}*s).

[0038] The membrane 16 is of a compact type, in other words having substantially no porosity, in which case the flow of the gas concerned through the membrane takes place by diffusion in the polymer matrix.

[0039] Membranes of the compact type having levels of permeability within the aforesaid limits may, for example, be based on silicone rubber such as vulcanized polydimethylsiloxane (PDMS) or poly(oxydimethylsilylene). Silicone rubbers have poor chemical compatibility with the polypropylene from which the sleeve 12 is preferably made, and therefore membranes made from this material are typically kept engaged in the sleeve 12 by the method described above with reference to Figures 1 and 2.

[0040] Additionally, if the material of the membrane is a silicone rubber, the membrane and the sleeve can be formed in one piece by a single moulding operation, forming a monolithic permeable element.

[0041] Other examples, provided for information and not intended to be exhaustive, of materials suitable for making membranes of the compact type include:

- polydienes and their copolymers, such as polybutadiene, polyisoprene, polyisoprene hydrochloride, polymethyl-1-pentenylene, hydrogenated polybutadiene, poly(2-methyl-1,3-pentadiene-co-4-methyl-1,3-pentadiene), vulcanized trans rubber, polychloroprene and butadiene-acrylonitrile copolymer;
- cellulose derivatives, such as ethylcellulose and cellulose acetobutyrate,
- styrene/olefin/diene-based copolymers such as styrene-ethylene-butene-styrene (SEBS) and styrene-ethylene-propylene-styrene (SEPS),
- polyoxides, such as poly(oxy-2,6-dimethyl-1,4-phenylene),
- polyolefins and their derivatives, such as low-density polyethylene or ethylene-vinylacetate copolymer (EVA),
- fluoridated polymers and copolymers, such as polytetrafluoroethylene and tetrafluoroethylene-hexafluoropropylene copolymer.

[0042] Some examples of membranes made from these materials are given in the table appended to the description.

[0043] The materials listed above are also more chemically compatible with polypropylene than are silicone rubbers, and they can therefore be overmoulded for the formation of the sleeve 12.

[0044] The membrane 16 can be of the composite type, formed by a single layer or by a plurality of superimposed layers, each of which can be made from any polymer, homopolymer, or polymer or copolymer mixture, which may be of a composite type and filled with inorganic filler. One of the layers can also consist of an inorganic, ceramic or zeolite material.

[0045] The materials forming the aforesaid membranes can be suitably nano-filled, for example with organomodified nanoclays, silica, TiO₂, magnesium oxide, titanium dioxide, etc., to achieve the desired oxygen permeability.

[0046] For microporous membranes (including nanoporous membranes), the membrane must, according to another aspect of the invention, have a molecular cut-off of less than 50 kDalton.

[0047] The molecular cut-off is a measurement correlated with the dimension of the micropores and indicates the maximum molecular weight of molecules capable of passing through the membrane by travelling through its holes.

[0048] The measurement of the dimension of the micropores is of considerable importance if the stopper 1 is used in bottles containing wine intended for a long maturing process. This is because a low molecular cut-off substantially impedes the passage of complex heavy molecules from and to the inside of the bottle, including molecules of compounds important for the conservation and/or production of the final flavour properties required in the wine contained in the bottle, and also including spores, moulds and bacteria.

[0049] In particular, the microporous membrane preferably has a molecular cut-off in the range from 1 to 30 kDalton, or more preferably in the range from 1 to 10 kDalton.

[0050] Microporous membranes having the characteristics specified above can be made, for example, from polytetrafluoroethylene (PTFE) and have a thickness ranging from 100 to 500 microns. Their chemical compatibility with polypropylene is also sufficient to enable them to be fixed to the sleeve 12 by an overmoulding method.

[0051] According to another aspect of the invention, the membrane 16 also preferably has a water vapour permeability, measured at 23°C, in the range from 50 to 500 g/m²d, a value at which the loss of water over time can be sufficiently controlled.

Examples

[0052] A set of stoppers were prepared according to the above teachings, using membranes with compact materials, with different permeability, and having different areas and thicknesses.

[0053] All the examples of stoppers made were tested under constant pressure and temperature, comparable with the environmental conditions in which the process of maturing a wine in the bottle normally takes place.

[0054] The test results are shown in Table 1, which lists the monthly flows of oxygen through a stopper having a membrane made from a material with a permeability indicated as Perm, a thickness indicated as S, in microns, and a specific diameter indicated as D, in mm.

[0055] The results which meet the flow requirements for a correct ageing process of the wine are those in the range from 0.1 to 2 mg/month, which, allowing for an oxygen exchange of approximately 0.1 mg/month through the tested stopper and the bottle neck, conform to the optimal exchange conditions for maturing a vintage wine.

[0056] All the materials used, the surface dimensions, the thicknesses and the measured oxygen flows are shown in Table 1 which is provided for the purposes of this description. The positive results, in other words those relating to a flow within the aforementioned range, are shown in bold type. The results in Table 1 demonstrate that silicone rubbers require greater thicknesses, in the region of 500 microns, in order to be suitable for the required purpose, while other polymer materials must have smaller thicknesses, of approximately 100 microns, or even as little as 10 microns.

[0057] A stopper 100 made according to a second example of the present invention is shown in Figure 3, in which details similar to details of the preceding example are identified by the same reference numerals.

[0058] In the stopper 100, the permeable element, in this case in the form of a membrane 101, is made from the same material as the main body 2, and is produced simultaneously with it, by a moulding method.

[0059] Clearly, this solution enables the production costs to be considerably reduced, since only one material and one operation are required, with no need for subsequent working or assembly.

[0060] This material must of course have not only the appropriate permeability but also all the necessary mechanical, chemical and physical, and workability characteristics for its use in the production of the main body 2.

[0061] A preferred example of this material consists of SEBS copolymer and SEPS copolymer. By using this material, it is possible to mould the main body 2, in one piece in a single operation, the passage 4, sealed by a membrane 16 of suitable thickness, being formed inside the main body. In particular, where the size of the passage 4 is approximately 7 mm, the membrane 16 has a thickness of approximately 1000 microns, which is large enough to allow the moulding method to be used.

[0062] In a third example of embodiment of the present invention, shown in Figure 4, which represents a stopper 200, the permeable element is of the insert type, in other words having a rod-like body 201 whose cross section is conjugate with that of the passage 4.

[0063] In this case, the predominant dimension of the permeable element is the axial dimension, which can be in the range from 2 mm to 60 mm, while the cross sections of the passage 4 are similar to those of the preceding example.

[0064] In this case, since the thickness of the permeable element is greater by approximately two orders of magnitude than the thickness of the membranes of the preceding example, the permeability required in the material forming the permeable element is, correspondingly, greater by approximately two orders of magnitude, being preferably in the range from 10⁻⁵ to 10⁻⁹ (Ncm³*cm/cm²*cmHg*s). Preferably, the insert is of the compact type.

[0065] Thus the present invention resolves the problem of the prior art identified above, while also offering numerous

other benefits.

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TABLE 1

Material	Perm Ncm ³ *c m/ (cm ² *cm Hg *s)	Oxygen flow (mg/month)										
		S=10μ D=1m m	S=10μ D=1.5m m	S=10μ D=2m m	S=100μ D=1mm	S=100μ D=1.5mm	S=100μ D=2mm	S=500μ D=1mm	S=500μ D=1.5mm	S=500μ D=2mm	S=250μ D=5mm	S=1000μ D=7mm
PDMS	8.00E-08	37.18	83.66	148.72	3.72	8.37	14.87	0.74	1.67	2.97	37.18	18.21
Poly (oxydimethylsilyl ene) with 10% Scantocel CS filler	4.88E-08	22.68	51.04	90.74	2.27	5.1	9.07	0.45	1.02	1.81	22.68	11.12
SEPS (Megol K)	1.88E-08	8.74	19.66	34.95	0.87	1.97	3.49	0.17	0.39	0.70	8.74	4.28
Polyisoprene hydrochloride	5.39E-09	2.50	5.63	10.01	0.25	0.56	1.00	0.05	0.11	0.20	2.50	1.23
Polymethyl-1- pentenylene	3.22E-09	1.50	3.37	5.98	0.15	0.34	0.60	0.03	0.07	0.12	1.50	0.73
Polyisoprene, amorphous	2.34E-09	1.09	2.45	4.35	0.11	0.24	0.44	0.02	0.05	0.09	1.09	0.53
Polybutadiene	1.90E-09	0.88	1.99	3.54	0.09	0.20	0.35	0.02	0.04	0.07	0.88	0.43
SEBS (Kraton G1650)	1.39E-09	0.64	1.44	2.57	0.06	0.14	0.26	0.01	0.03	0.05	0.64	0.32
SEBS (Kraton G2705)	2.51E-09	1.16	2.62	4.66	0.12	0.26	0.47	0.02	0.05	0.09	1.16	0.57
Poly(oxy-2,6- dimethyl-1,4- phenylene)	1.58E-09	0.74	1.66	2.94	0.07	0.17	0.29	0.01	0.03	0.06	0.74	0.36
Ethyl cellulose	1.46E-09	0.68	1.53	2.73	0.07	0.15	0.27	0.01	0.03	0.05	0.68	0.33

(continued)

Material	Perm Ncm ³ *c m/ (cm ² *cm Hg*s)	Oxygen flow (mg/month)										
		S=10μ D=1m m	S=10μ D=1.5m m	S=10μ D=2m m	S=100μ D=1mm	S=100u D=1.5mm	S=100μ D=2mm	S=500μ D=1mm	S=500μ D=1.5mm	S=500μ D=2mm	S=250μ D=5mm	S=1000μ D=7mm
Hydrogenated polybutadiene	1.13E-09	0.52	1.18	2.10	0.05	0.12	0.21	0.01	0.02	0.04	0.52	0.26
Poly (2-methyl-1,3-pentadiene-co-4-methyl-1,3-pentadiene) 85/15	1.00E-09	0.46	1.05	1.86	0.05	0.10	0.19	0.01	0.02	0.03	0.46	0.23
Polybutadiene-co-acrylonitrile 80/20	8.18E-10	0.38	0.86	1.52	0.04	0.09	0.15	0.01	0.02	0.03	0.38	0.19
Purified vulcanized trans rubber, gutta percha	6.17E-10	0.29	0.65	1.15	0.03	0.06	0.11	0.01	0.01	0.02	0.29	0.14
Polytetrafluoroethylene-co-hexafluoropropylene	4.89E-10	0.23	0.51	0.91	0.02	0.05	0.09	0.00	0.01	0.02	0.23	0.11
Cellulose acetobutyrate	4.73E-10	0.22	0.50	0.88	0.02	0.05	0.09	0.00	0.01	0.02	0.22	0.11
Polytetrafluoroethylene (PTFE)	4.26E-10	0.20	0.45	0.79	0.02	0.04	0.08	0.00	0.01	0.02	0.20	0.10
Fluorinated polymer	4.22E-10	0.20	0.44	0.78	0.02	0.04	0.08	0.00	0.01	0.01	0.20	0.10
Polychloroprene	3.94E-10	0.18	0.41	0.73	0.02	0.04	0.07	0.00	0.01	0.01	0.18	0.09

(continued)

Material	Perm Ncm ³ *c m/ (cm ² *cm Hg*s)	Oxygen flow (mg/month)										
		S=10μ D=1m m	S=10μ D=1.5m m	S=10μ D=2m m	S=100μ D=1mm	S=100u D=1.5mm	S=100μ D=2mm	S=500μ D=1mm	S=500μ D=1.5mm	S=500μ D=2mm	S=250μ D=5mm	S=1000μ D=7mm
Polybutadiene- co-acrylonitrile 73/27	3.86E- 10	0.18	0.40	0.72	0.02	0.04	0.07	0.00	0.01	0.01	0.18	0.09
LDPE (low- density polyethylene)	2.93E- 10	0.14	0.31	0.54	0.01	0.03	0.05	0.00	0.01	0.01	0.14	0.07

Claims

1. Stopper (1, 100, 200) for sealing bottles (3), particularly for sealing bottles of wine for ageing, comprising:

- a main body (2) shaped in such a way as to be removably housed in engagement in an aperture (3a) of the said bottles,
- a first surface (5) and a second surface (6) formed on the said main body and facing, respectively, the outside and the inside of the said bottles when the said main body is received in engagement in the said aperture,
- at least one passage (4) extending between the said first and second surfaces and capable of making the inside of the said bottles communicate with the environment outside the bottles,

wherein the stopper comprises a permeable element (16, 101, 201) which is impermeable to liquids and permeable to oxygen, the said permeable element being extended to seal the said passage in order to regulate the flow of oxygen between the inside and the outside of the bottle, the said permeable element having an oxygen permeability, measured at 20°C, in the range from 10^{-7} to 10^{-11} ($\text{Ncm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{cm}_{\text{Hg}} \cdot \text{s}$) **characterised in that** said permeable element is of the compact type, having substantially no porosity and in which the flow of oxygen takes place by diffusion.

2. Stopper according to Claim 1, in which said permeable element comprises at least one membrane (16) having an oxygen permeability, measured at 20°C, in the range from 10^{-7} to 10^{-11} ($\text{Ncm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{cm}_{\text{Hg}} \cdot \text{s}$).

3. Stopper according to Claim 2, in which the said membrane is of the compact type and is made from a material selected from a group composed of silicone rubbers, polydienes and their copolymers, cellulose derivatives, styrene/olefin/diene-based copolymers, polyoxides, polyolefins and their derivatives, and fluoridated polymers and copolymers.

4. Stopper according to Claim 3, in which the said membrane is made from a material selected from a group composed of polybutadiene, polyisoprene, polyisoprene hydrochloride, polymethyl-1-pentenylene, ethyl cellulose, styrene-ethylene-butene-styrene copolymer (SEBS), styrene-ethylene-propylene-styrene copolymer (SEPS), poly(oxy-2,6-dimethyl-1,4-phenylene), hydrogenated polybutadiene, poly(2-methyl-1,3-pentadiene-co-4-methyl-1,3-pentadiene), butadiene-acrylonitrile copolymer, vulcanized trans rubber, tetrafluoroethylene-hexafluoropropene copolymer, cellulose acetobutyrate, fluoridated polymers such as polytetrafluoroethylene, polychloroprene, low-density polyethylene, and ethylene vinylacetate copolymer (EVA).

5. Stopper according to Claim 4, in which the said membrane is based on silicone rubber, SEBS, SEPS or EVA.

6. Stopper according to any one or more of Claims 2 to 5, in which the said at least one membrane has a total equivalent area for the passage of oxygen, the said total equivalent area being in the range from 0.0078 to 78.5 mm^2 .

7. Stopper according to Claim 6, in which the said total equivalent area is in the range from 0.78 to 38.5 mm^2 .

8. Stopper according to any one or more of the preceding claims, in which the said at least one membrane has a total equivalent thickness of the area through which oxygen passes, the said total equivalent thickness being in the range from 5 to 2000 microns.

9. Stopper according to Claim 8, in which the said total equivalent thickness is in the range from 10 to 1000 microns.

10. Stopper according to any one or more of the preceding claims, in which the said membrane has a water vapour permeability measured at 23°C in the range from 50 to 500 ($\text{g} / \text{m}^2 \cdot \text{d}$).

11. Stopper according to any one or more of Claims 3 to 10, in which the said main body (2) and the said membrane (101) are made in one piece from the same material.

12. Stopper according to Claim 11, in which the said main body and the said membrane are made from SEBS copolymer or from SEPS copolymer or from EVA.

13. Stopper according to any one or more of Claims 2 to 12, in which the said membrane is fixed in a support sleeve (12) which in turn is fixed inside the said passage.

14. Stopper according to Claim 13, in which a seat (8) for housing the said support sleeve is provided the said passage.
15. Stopper according to Claim 14, in which the said seat is longitudinally delimited by a bead (10) extending radially from the said main body towards the said passage, and by a shoulder (11) formed in the said passage.
16. Stopper according to any one or more of Claims 13 to 15, in which the said sleeve (12) has a profile tapered along a longitudinal axis (X) of the said passage.
17. Stopper according to any one or more of Claims 13 to 16, in which the said sleeve comprises a projection (19) extending radially around its outer shell so as to increase the security of fixing between the said sleeve (12) and the said main body (2).
18. Stopper according to Claim 17, in which the said sleeve has a truncated conical profile and the said projection extends from the major base (13) of the said sleeve.
19. Stopper according to Claim 18, in which the said projection has a sharp edge facing the walls of the said passage.
20. Stopper according to any one or more of Claims 13 to 19, in which the said membrane is fixed in the said support sleeve by overmoulding the said sleeve on to the said membrane.
21. Stopper according to any one or more of Claims 13 to 19, in which the said membrane is made in one piece with the said support sleeve.
22. Stopper according to Claim 1, in which the said permeable element comprises an insert (201) with a predominant axial dimension, having an oxygen permeability measured at 20°C in the range from 10^{-5} to 10^{-9} ($\text{Ncm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{cm}_{\text{Hg}} \cdot \text{s}$).
23. Stopper according to Claim 22, in which the said insert has a total equivalent area in the range from 0.7 to 78.5 mm^2 and a total equivalent thickness in the range from 2 to 60 millimetres.

Patentansprüche

1. Stopfen (1, 100, 200) zum Abdichten von Flaschen (3), insbesondere zum Abdichten von Weinflaschen für einen Alterungsprozess, umfassend:
 - einen Hauptkörper (2), der so geformt ist, dass er herausnehmbar in Eingriff in einer Öffnung (3a) der Flaschen untergebracht ist,
 - eine erste Oberfläche (5) und eine zweite Oberfläche (6), die auf dem Hauptkörper ausgebildet sind und jeweils der Außenseite und der Innenseite der Flaschen zugewandt sind, wobei der Hauptkörper in Eingriff in der Öffnung aufgenommen wird,
 - zumindest einen Durchgang (4), der sich zwischen der ersten und zweiten Oberfläche erstreckt und dafür sorgt, dass die Innenseite der Flaschen mit der Umgebung außerhalb der Flaschen in Verbindung steht,
- wobei der Stopfen ein durchlässiges Element (16, 101, 201) umfasst, das für Flüssigkeiten undurchlässig und für Sauerstoff durchlässig ist, wobei sich das durchlässige Element erstreckt, um den Durchgang abzudichten, um den Sauerstoffdurchfluss zwischen der Innenseite und der Außenseite der Flasche zu regulieren, wobei das durchlässige Element eine Sauerstoffdurchlässigkeit im Bereich von 10^{-7} bis 10^{-11} ($\text{Ncm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{cm}_{\text{Hg}} \cdot \text{s}$), gemessen bei 20° C, aufweist, **dadurch gekennzeichnet, dass** das durchlässige Element von kompakter Art ist, die im Wesentlichen keine Porosität aufweist und bei der der Sauerstoffdurchfluss durch Diffusion stattfindet.
2. Stopfen nach Anspruch 1, wobei das durchlässige Element zumindest eine Membran (16) umfasst, die eine Sauerstoffdurchlässigkeit im Bereich von 10^{-7} bis 10^{-11} ($\text{Ncm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{cm}_{\text{Hg}} \cdot \text{s}$), gemessen bei 20° C, aufweist.
3. Stopfen nach Anspruch 2, wobei die Membran von kompakter Art und aus einem Material gefertigt ist, ausgewählt aus einer Gruppe bestehend aus Silikongummis, Polydienen und deren Copolymeren, Zellosederivaten, Styrol-/Olefin-/Dien-basierten Copolymeren, Polyoxiden, Polyolefinen und deren Derivaten, und fluorisierten Polymeren und Copolymeren.

4. Stopfen nach Anspruch 3, wobei die Membran aus einem Material gefertigt ist, ausgewählt aus einer Gruppe bestehend aus Polybutadien, Polyisopren, Polyisopren-Hydrochlorid, Polymethyl-1-Pentenyl, Ethylzellulose, Styrol-Ethylen-Buten-Styrol-Copolymer (SEBS), Styrol-Ethylen-Propylen-Styrol-Copolymer (SEPS), Poly(oxy-2,6-Dimethyl-1,4-Phenyl), hydriertes Polybutadien, Poly(2-Methyl-1,3-Pentadien-co-4-Methyl-1,3-Pentadien), Butadien-Acrylnitril-Copolymer, vulkanisierter Transgummi, Tetrafluorethylen-Hexafluorpropen-Copolymer, Zellulose-Aceto-
butyrat, fluorisierte Polymere, wie Polytetrafluorethylen, Polychloropren, Polyethylen niedriger Dichte, und Ethylen-
vinylacetat-Copolymer (EVA).
5. Stopfen nach Anspruch 4, wobei die Membran auf Silikongummi, SEBS, SEPS oder EVA basiert.
6. Stopfen nach einem oder mehreren der Ansprüche 2 bis 5, wobei die zumindest eine Membran einen Gesamtäquivalenzfläche für den Durchfluss von Sauerstoff aufweist, wobei die Gesamtäquivalenzfläche im Bereich von 0,0078 bis 78,5 mm² liegt.
7. Stopfen nach Anspruch 6, wobei die Gesamtäquivalenzfläche im Bereich von 0,78 bis 38,5 mm² liegt.
8. Stopfen nach einem oder mehreren der vorstehenden Ansprüche, wobei die zumindest eine Membran eine Gesamtäquivalenzdicke der Fläche, durch welche Sauerstoff hindurchtritt, aufweist, wobei die Gesamtäquivalenzdicke im Bereich von 5 bis 2000 Mikrometer liegt.
9. Stopfen nach Anspruch 8, wobei die Gesamtäquivalenzdicke im Bereich von 10 bis 1000 Mikrometer liegt.
10. Stopfen nach einem oder mehreren der vorstehenden Ansprüche, wobei die Membran eine Wasserdampfdurchlässigkeit im Bereich von 50 bis 500 (g/m²d), gemessen bei 23°C, aufweist.
11. Stopfen nach einem oder mehreren der Ansprüche 3 bis 10, wobei der Hauptkörper (2) und die Membran (101) in einem Stück aus dem gleichen Material gefertigt sind.
12. Stopfen nach Anspruch 11, wobei der Hauptkörper und die Membran aus SEBS-Copolymer oder aus SEPS-Copolymer oder aus EVA gefertigt sind.
13. Stopfen nach einem oder mehreren der Ansprüche 2 bis 12, wobei die Membran in einer Lagerhülse (12) befestigt ist, die wiederum innerhalb des Durchgangs befestigt ist.
14. Stopfen nach Anspruch 13, wobei eine Aufnahme (8) zum Aufnehmen der Lagerhülse in dem Durchgang vorgesehen ist.
15. Stopfen nach Anspruch 14, wobei die Aufnahme in Längsrichtung durch eine Leiste (10), die sich radial vom Hauptkörper in Richtung zum Durchgang erstreckt, und durch eine Schulter (11), die in dem Durchgang ausgebildet ist, begrenzt wird.
16. Stopfen nach einem oder mehreren der Ansprüche 13 bis 15, wobei die Hülse (12) ein Profil aufweist, das sich entlang einer Längsachse (X) des Durchgangs verjüngt.
17. Stopfen nach einem oder mehreren der Ansprüche 13 bis 16, wobei die Hülse einen Vorsprung (19) umfasst, der sich radial um deren Außenmantel erstreckt, um so die Befestigungssicherheit zwischen der Hülse (12) und dem Hauptkörper (2) zu erhöhen.
18. Stopfen nach Anspruch 17, wobei die Hülse ein kegelstumpfförmiges Profil aufweist und der Vorsprung sich von der Hauptbasis (13) zur Hülse erstreckt.
19. Stopfen nach Anspruch 18, wobei der Vorsprung eine scharfe Kante aufweist, die den Wänden des Durchgangs zugewandt ist.
20. Stopfen nach einem oder mehreren der Ansprüche 13 bis 19, wobei die Membran in der Lagerhülse befestigt ist, indem die Hülse auf der Membran mit Übermaß ausgeformt ist.
21. Stopfen nach einem oder mehreren der Ansprüche 13 bis 19, wobei die Membran in einem Stück mit der Lagerhülse

gefertigt ist.

22. Stopfen nach Anspruch 1, wobei das durchlässige Element einen Einsatz (201) mit einer vorwiegend axialen Abmessung umfasst, der eine Sauerstoffdurchlässigkeit im Bereich von 10^{-5} bis 10^{-9} ($\text{Ncm}^3\text{cm}/\text{cm}^2\text{cm}_{\text{Hg}}^*\text{s}$), gemessen bei 20°C , aufweist,

23. Stopfen nach Anspruch 22, wobei der Einsatz eine Gesamtäquivalenzfläche im Bereich von 0,7 bis $78,5\text{ m}^2$ und eine Gesamtäquivalenzdicke im Bereich von 2 bis 60 mm aufweist.

Revendications

1. Bouchon (1, 100, 200) pour fermer hermétiquement des bouteilles (3), particulièrement pour fermer hermétiquement des bouteilles de vin pour le vieillissement, comprenant :

- un corps principal (2) conformé d'une telle manière qu'il est abrité en engagement dans une ouverture (3a) desdites bouteilles, tout en pouvant être enlevé,
- une première surface (5) et une seconde surface (6) formées sur ledit corps principal et faisant respectivement face vers l'extérieur et vers l'intérieur desdites bouteilles quand ledit corps principal est reçu en engagement dans ladite ouverture,
- au moins un passage (4) s'étendant entre ladite première et ladite seconde surface et capable d'amener l'intérieur desdites bouteilles à communiquer avec l'environnement à l'extérieur des bouteilles,

dans lequel le bouchon comprend un élément perméable (16, 101, 201) qui est imperméable aux liquides et perméable à l'oxygène, ledit élément perméable s'étendant pour fermer hermétiquement ledit passage afin de réguler le débit d'oxygène entre l'intérieur et l'extérieur de la bouteille, ledit élément perméable ayant une perméabilité à l'oxygène, mesurée à 20°C , dans la plage de 10^{-7} à 10^{-11} ($\text{Ncm}^3\text{cm}/\text{cm}^2\text{cm}_{\text{Hg}}^*\text{s}$), **caractérisé en ce que** ledit élément perméable est du type compact n'ayant sensiblement pas de porosité et dans lequel l'écoulement d'oxygène se produit par diffusion.

2. Bouchon selon la revendication 1, dans lequel ledit élément perméable comprend au moins une membrane (16) ayant une perméabilité à l'oxygène, mesurée à 20°C , dans la plage de 10^{-7} à 10^{-11} ($\text{Ncm}^3\text{cm}/\text{cm}^2\text{cm}_{\text{Hg}}^*\text{s}$).

3. Bouchon selon la revendication 2, dans lequel ladite membrane est du type compact et est réalisée d'un matériau choisi parmi un groupe composé de caoutchouc aux silicones, polydiènes et leurs copolymères, dérivés de cellulose, copolymères à base styrène/oléfine/diène, polyoxydes, polyoléfines et leurs dérivés, et les polymères fluorés et leurs copolymères.

4. Bouchon selon la revendication 3, dans lequel ladite membrane est réalisée en un matériau choisi parmi un groupe composé de polybutadiène, polyisoprène, polyisoprène hydrochlorure, polyméthyl-1-penténylène, éthyle cellulose, copolymère styrène-éthylène-butène-styrène (SEBS), copolymère styrène-éthylène-propylène-styrène (SEPS), poly(oxy-2,6-diméthyl-1,4-phénylène), polybutadiène hydrogéné, poly(2-méthyl-1,3-pentadiène-co-4-méthyle-1,3-pentadiène), copolymère butadiène-acrylonitrile, trans-caoutchouc vulcanisé, copolymère tétrafluoroéthylène-hexafluoropropane, cellulose acétobutyrate, polymères fluorés comme polytétrafluoroéthylène, polychloroprène, polyéthylène basse densité, et copolymère éthylène-vinyle acétate (EVA).

5. Bouchon selon la revendication 4, dans lequel ladite membrane est basée sur du caoutchouc aux silicones, SEBS, SEPS ou EVA.

6. Bouchon selon l'une quelconque ou plusieurs des revendications 2 à 5, dans lequel ladite au moins une membrane présente une superficie équivalente totale pour le passage d'oxygène, ladite superficie équivalente totale étant dans la plage de $0,0078$ à $78,5\text{ mm}^2$.

7. Bouchon selon la revendication 6, dans lequel ladite superficie équivalente totale est dans la plage de $0,78$ à $38,5\text{ mm}^2$.

8. Bouchon selon l'une quelconque ou plusieurs des revendications précédentes, dans lequel ladite au moins une membrane présente une épaisseur équivalente totale de la zone à travers laquelle passe l'oxygène, ladite épaisseur

équivalente totale étendant la plage de 5 à 2000 microns.

9. Bouchon selon la revendication 8, dans lequel ladite épaisseur équivalente totale est dans la plage de 10 à 1000 microns.

10. Bouchon selon l'une quelconque ou plusieurs des revendications précédentes, dans lequel ladite membrane présente une perméabilité à la vapeur d'eau, mesurée à 23°C, dans la plage de 50 à 500 (g/m²d).

11. Bouchon selon l'une quelconque ou plusieurs des revendications 3 à 10, dans lequel ledit corps principal (2) et ladite membrane (101) sont formés d'une seule pièce à partir du même matériau.

12. Bouchon selon la revendication 11, dans lequel ledit corps principal et ladite membrane sont réalisés de copolymère SEBS, ou de copolymère SEPS ou de EVA.

13. Bouchon selon l'une quelconque ou plusieurs des revendications 2 à 12, dans lequel ladite membrane est fixée dans un fourreau de support (12) qui est à son tour fixé à l'intérieur dudit passage.

14. Bouchon selon la revendication 13, dans lequel un siège (8) pour loger ledit fourreau de support est prévu dans ledit passage.

15. Bouchon selon la revendication 14, dans lequel ledit siège est délimité longitudinalement par un bourrelet (10) s'étendant à radialement depuis ledit corps principal vers ledit passage, et par un épaulement (11) formé dans ledit passage.

16. Bouchon selon l'une quelconque ou plusieurs des revendications 13 à 15, dans lequel ledit manchon (12) a un profil effilé et le long d'un axe longitudinal (X) dudit passage.

17. Bouchon selon l'une quelconque ou plusieurs des revendications 13 à 16, dans laquelle ledit manchon comprend une projection (19) s'étendant à radialement autour de sa coque extérieure de manière augmenter la sécurité de fixation entre ledit manchon (12) et ledit corps principal (2).

18. Bouchon selon la revendication 17, dans lequel ledit manchon présente un profil en tronc de cône et ladite projection s'étend depuis la grande base (13) dudit manchon.

19. Bouchon selon la revendication 18, dans lequel ladite projection présente un bord vif en face des parois dudit passage.

20. Bouchon selon l'une quelconque ou plusieurs des revendications 13 à 19, dans lequel ladite membrane est fixée dans ledit manchon de support par surmoulage dudit manchon sur ladite membrane.

21. Bouchon selon l'une quelconque ou plusieurs des revendications 13 à 19, dans lequel ladite membrane est réalisée d'une seule pièce avec ledit manchon de support.

22. Bouchon selon la revendication 1, dans lequel ledit élément perméable comprend un insert (201) avec une dimension axiale prédominante, ayant une perméabilité à l'oxygène mesurée à 20°C dans la plage de 10⁻⁵ à 10⁻⁹ (Ncm³*cm/cm²*cm_{Hg} *s).

23. Bouchon selon la revendication 22, dans lequel ledit insère présente une superficie équivalente totale dans la plage de 0,7 à 78,5 mm² et une épaisseur équivalente totale dans la plage de 2 à 60 mm.

Fig. 1

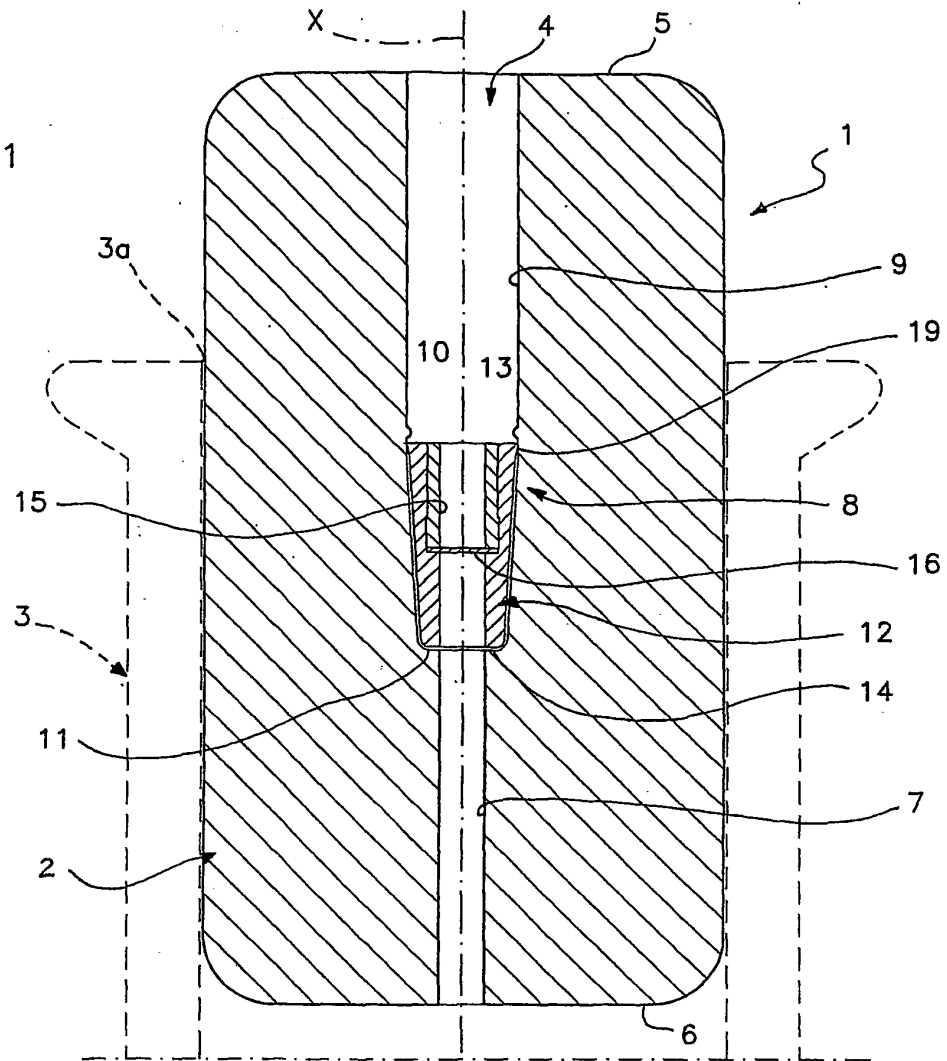
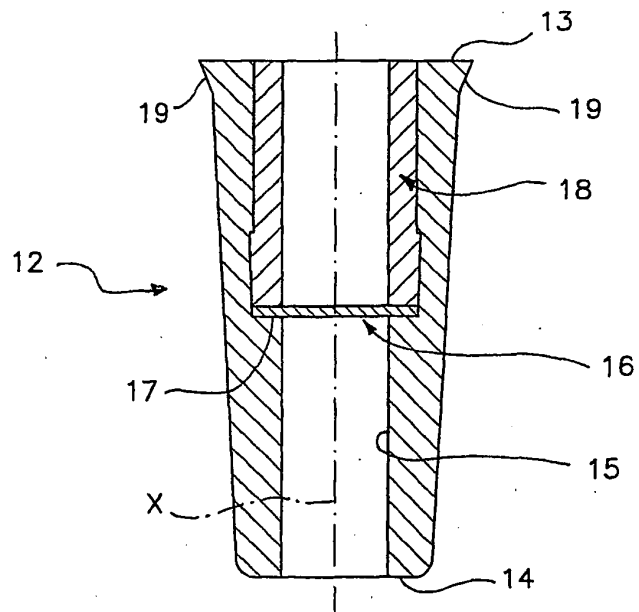
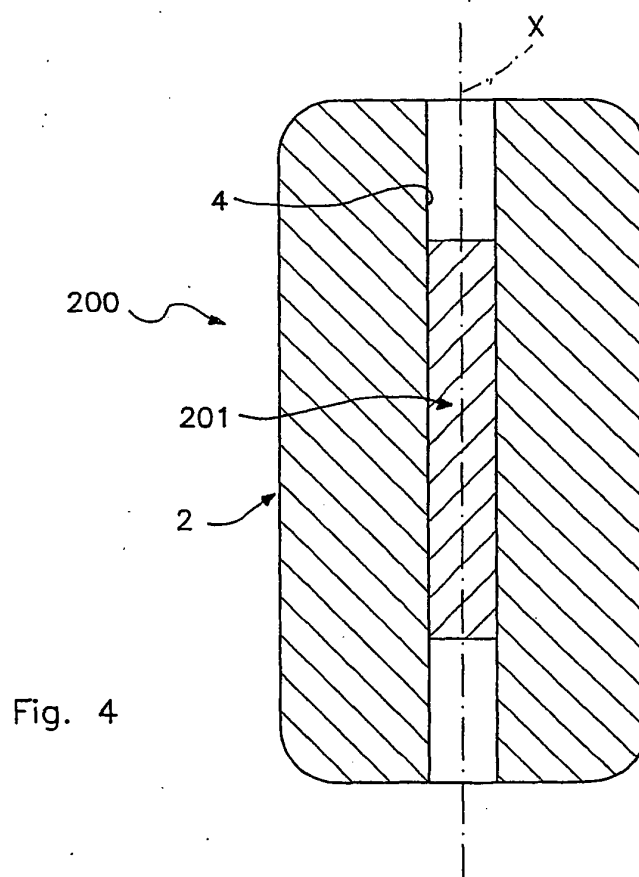
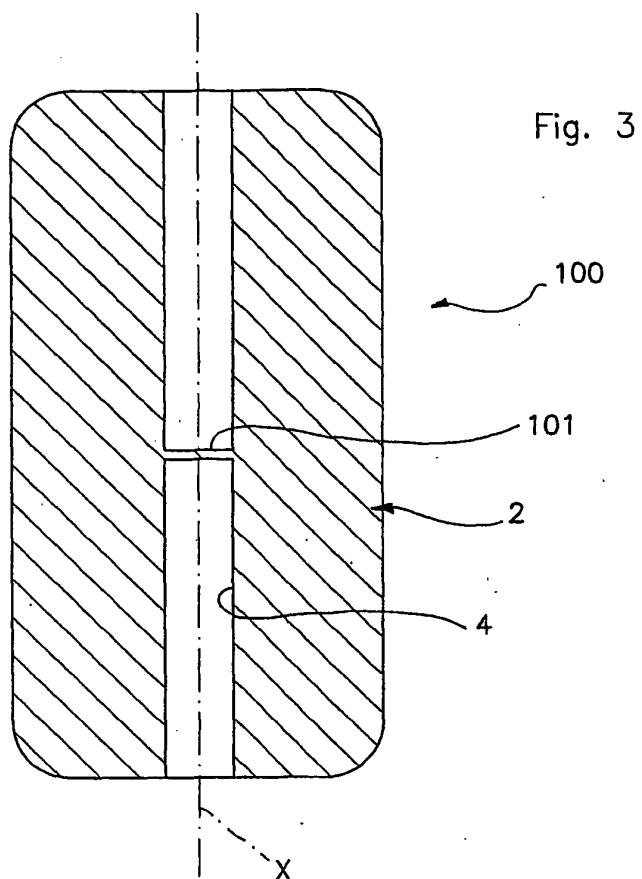


Fig. 2





REFERENCES CITED IN THE DESCRIPTION

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