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(71) Applicant  
Nitto Electric Industrial  
Co. Ltd., No. 1—2,  
Shimohozumi 1-chome,  
Ibaraki-shi, Osaka, Japan  
(72) Inventors  
Kanji Kawakami,  
Yasuhiro Moriyama,  
Takafumi Okamoto  
(74) Agent  
Marks & Clerk

(54) **Producing a Porous  
Polytetrafluoroethylene Article**

(57) A porous P.T.F.E. article (e.g. a rod, tube or film) is produced by shaping a mixture of P.T.F.E. powder and a liquid lubricant and, optionally, a foaming agent by extrusion and/or rolling, and then heating the article 1 in

a heating zone 3 to a temperature of at least the melting point of the P.T.F.E. whilst stretching the article 1 using pinch rolls 4 and 5 disposed outside the heating zone 3. The article 1 may be stretched transversely and/or longitudinally. The stretched article 1 is cooled and is then preferably heat treated whilst maintaining the stretching ratio.

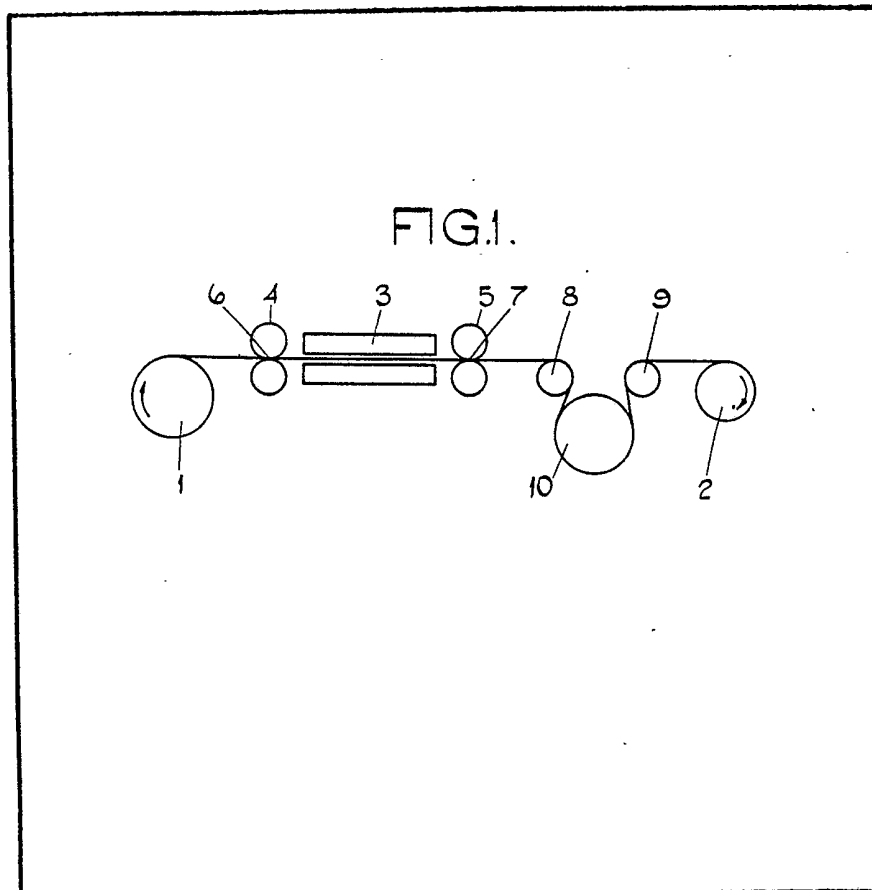


FIG.1.

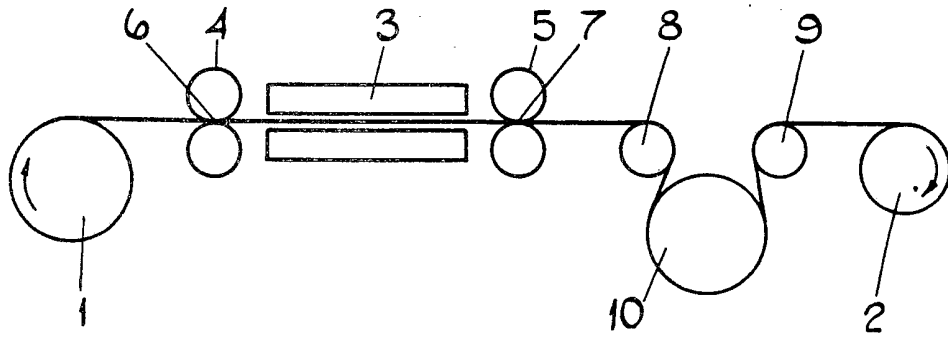
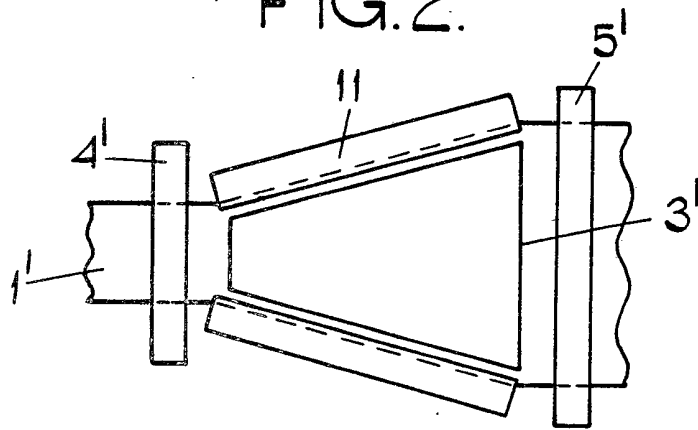


FIG.2.



## SPECIFICATION

**Process for Producing a Porous Polytetrafluoroethylene Body**

This invention relates to a process for producing a sintered porous polytetrafluoroethylene body.

5 Polytetrafluoroethylene (hereinafter referred to as "PTFE") is an industrially important material because it has excellent thermal stability, chemical resistance, mechanical characteristics (e.g. tensile strength and wear resistance) and electrical insulation properties. Porous PTFE bodies have found a wide range of applications, for example, as filters for strongly corrosive materials, as cell diaphragms, and as separation diaphragms for separation of isotopes such as uranium hexafluoride. 5

10 Generally, a porous body of a thermoplastic resin is produced by adding a foaming agent to the resin, and melting the mixture to decompose the foaming agent thereby to expand the resin. However, it is very difficult in practice to obtain a porous PTFE article by this process because PTFE has a high melt viscosity and is scarcely flowable even when heated to its melting point (about 327°C) or higher and, therefore, the effect of the foaming agent cannot be fully used. 10

15 A porous PTFE body is generally produced by mixing PTFE powder and an organic or inorganic fine powder which can be eluted from the molded body, molding the resulting mixture into a desired shape and eluting the fine powder from the molded article. However, this elution method has the problem that due to the porous state, the organic or inorganic powders cannot completely be eluted, some fine powder tends to be retained in the article and the residual fine powder deteriorates the basic mechanical characteristics and, electrical insulation properties for example of the PTFE. 15

20 To overcome the above problem, a method has been proposed to produce the porous PTFE article by molding a mixture of a PTFE powder and a liquid lubricant such as naphtha, and stretching the molded article at a temperature below the melting point of PTFE thereby to render it porous. However, the product which is unsintered has a low mechanical strength and stretches, cuts or breaks under a slight external force, and thus frequently presents problems in use. 20

25 To overcome the above problem, the stretched unsintered product is usually sintered at the melting temperature of PTFE or higher while maintaining the article in the stretched state to increase its mechanical strength. According to this method, it is certainly possible to obtain a porous article having a high mechanical strength, however, the number of manufacturing steps increases, and the manufacturing apparatus becomes complicated. Moreover, an energy consumption during manufacturing also increases greatly. It is urgently desired to overcome these difficulties. 25

30 According to the present invention, there is provided a process for producing a porous polytetrafluoroethylene body which comprises the steps of shaping a mixture of a polytetrafluoroethylene powder and a liquid lubricant by extrusion and/or rolling to form an article of the desired shape, disposing the shaped article in a heating zone such that two extremities of the shaped article on an axis in a direction in which the shaped article is to be stretched are located outside the heating zone, heating the portion of the molded article which is within the heating zone at a temperature of the melting point of the polytetrafluoroethylene or higher, and simultaneously stretching the heated molded article in at least one direction. 30

35 It has been found that a porous body of PTFE having a relatively high porosity can be obtained by incorporating a foaming agent in the mixture to accelerate formation of micropores upon stretching. 35

A porous PTFE body having an especially good dimensional stability can be obtained by heat-treating the porous body after stretching while maintaining it in the stretched state.

In the accompanying drawings:—

45 Figure 1 is a schematic side view of an apparatus for use in a process for producing a porous PTFE body in accordance with the present invention. 45

Figure 2 is a schematic plan view showing the principle parts of another apparatus for use in a process for producing a porous PTFE body in accordance with the present invention.

50 The molded PTFE body is obtained by first mixing a PTFE powder and a liquid lubricant and optionally a foaming agent and shaping the mixture using at least one of extrusion and rolling to obtain an article of the desired shape, such as a rod, tube or film corresponding to the desired final shape of the porous PTFE body. Compression molding can also be performed in addition to extrusion and/or rolling molding. 50

55 The liquid lubricant is a material which can wet the surface of PTFE powder as disclosed in, for example, U.S. Patent 3,002,770 and can be removed by for example heating (evaporation) or, extraction, after the preparation of the molded article. Specific examples of the liquid lubricants include hydrocarbon oils, such as liquid paraffin, naphtha or white oil, aromatic hydrocarbons, such as toluene or xylene, alcohols, ketones, esters, silicone oils, fluorochlorocarbon oils, solutions of polymers, such as polyisobutylene or polyisoprene in these solvents, mixtures of two or more of these, and water or aqueous solutions containing surface active agents. 55

60 The amount of the liquid lubricant which is mixed with the PTFE powder depends, for example, upon the method of obtaining the molded article, and the presence or absence of other additives, but is usually 5 to 50 parts by weight, preferably 10 to 30 parts by weight, per 100 parts by weight of the PTFE powder. 60

The foaming agent when used may be an organic or an inorganic foaming agent. Specific

examples of organic foaming agents include azo-type foaming agents e.g. azodicarbon amide, azobisisobutyronitrile, barium azodicarbonate, diethyl azodicarboxylate, diazoaminobenzene and azocyclohexyl nitrile, hydrazide-type foaming agents, e.g. p-toluenesulfonyl hydrazide, benzenesulfonyl hydrazide and p,p'-oxybisbenzenesulfonyl hydrazide, semicarbazide-type foaming agents, e.g. p,p'-oxybisbenzenesulfonyl semi-carbazide and p-toluenesulfonyl semicarbazide and nitroso-type foaming agents e.g. N,N'-dinitrosopentamethylene tetramine and N,N'-dimethyl-N,N'-dinitrosoterephthal amide. Specific examples of inorganic foaming agents include ammonium carbonate, sodium bicarbonate and, ammonium nitrile. These organic or inorganic foaming agents can be used individually or as a mixture thereof.

10 The amount of the foaming agent which is mixed with the PTFE powder depends, for example, on the desired porosity of the porous PTFE article, and the stretching ratio at the subsequent stretching step, but is usually up to 15 parts by weight per 100 parts by weight of the PTFE powder. If the amount of the foaming agent exceeds 15 parts by weight, the processability of the mixture decreases and the formation of the shaped article becomes difficult, and also a part of the foaming agent tends to be retained in the porous PTFE body. In view of the processability and the like, an amount of 1 to 5 parts by weight foaming agent is especially preferred.

In addition to the foaming agent, a foaming assistant e.g. urea, ethanolamine, oxalic acid, succinic acid or citric acid can be used to control the decomposition temperature, decomposition rate and amount of gas generated by the foaming agent.

20 In mixing the liquid lubricant and optionally the foaming agent with the PTFE powder, various additives, for example, pigments for coloration, and carbon black, graphite silica powder, asbestos powder, glass powder, metal powders, metal oxide powders, and metal sulfide powders for increasing strength to compression, improving abrasion resistance, and preventing cold flow, can be used in a conventional manner.

25 The article thus-obtained is then subjected to further processing. In most cases, in the practice of the present invention, the liquid lubricant is removed prior to subsequent processing by heating, extraction, or a combination of these. If desired, it is also possible to remove the liquid lubricant during or after the heating step.

30 In the heating step of the process of this invention where the foaming agent is not used, the article is disposed in a heating zone in such a manner that two extremities (ends) on an axis in the direction in which the molded article is stretched are outside the heating zone. Then, that portion of the article which is located within the heating zone is heated and sintered at a temperature of the melting point of PTFE or higher and, at the same time, the article is stretched in at least one direction using both extremities as base points. Thus, a sintered porous PTFE body is obtained in which numerous micropores are formed.

35 Further, where the foaming agent is used: (a) the article is disposed in a heating zone in such a manner that both ends in the direction in which the article is stretched are outside the heating zone, the portion of the article which is located within the heating zone is heated and sintered at a temperature of the melting point of PTFE or higher to decompose the foaming agent and at the same time, the article is stretched in at least one direction with the both ends used as base points, or (b) the article is previously heated to the decomposition temperature of the foaming agent or higher, preferably at a temperature between the decomposition temperature of the foaming agent and the melting point of PTFE, to decompose the foaming agent and subsequently the article is treated in the same manner as in (a) above. Thus, a sintered porous PTFE body is obtained in which numerous micropores are formed.

45 In the case of the method (a) above, numerous micropores are formed by a synergistic effect of the decomposition of the foaming agent and the stretching of the article and simultaneously the article is sintered. In the case of the method (b) above, the pore diameter of the numerous micropores formed in the molded article by decomposition of the foaming agent is expanded and new micropores are formed by stretching while sintering. Therefore, method (b) is more advantageous in forming micropores than method (a).

In stretching the article, a large force is exerted on both ends or extreme portions of the article. Thus, the purpose of placing these portions outside the heating zone in the heating step is to prevent their softening or melting during stretching.

55 Heating of that portion of the article which is located within the heating zone is carried out at the melting point of PTFE or higher. To perform sintering uniformly within a short period of time and to prevent heat degradation, it is preferred to perform the heating at 340°C to 410°C.

60 During the heating and stretching step, while a portion of the article within the heating zone is heated and sintered, it is stretched in at least one direction. Stretching is effected for the purpose of forming numerous micropores. The stretching ratio is determined according to the desired porosity and pore diameter of the final PTFE porous body, the direction of stretching, the number of directions in which the stretching is performed, etc. Usually, the stretching ratio is 10% to 1,000%. In view of the micropore forming effect by stretching, the uniformity of the pore sizes of the micropores, etc., the preferred stretching ratio is 20% to 700%.

65 When the stretching is carried out in one direction, the formation of micropores at the time of

stretching can be facilitated by also locating outside the heating zone two other extremities of the article on an axis perpendicular to the axis in which the article is stretched, or by fixing such ends in the heating zone by chucks or clips, for example, so that the distance between these two ends does not change. When stretching is carried out in more than one direction, for example, stretching as shown in Figure 2 discussed below, extremities on the axes in each direction in which the molded article is stretched are located outside the heating zone.

The porosity and pore diameter of the porous body obtained depend on the stretching ratio, the direction of stretching, the number of stretching axes, the sintering temperature, etc. Usually, the porosity is 35% to 95%, and the pore diameter is 0.01 to 100 microns.

In another embodiment of this invention, the sintered article (porous body) is further heat-treated while it is maintained in the stretched state, that is, while maintaining the length of the article in the stretched direction. As a result of this heat-treatment, the stretched state of the porous sintered body can be set and the resulting product has especially good dimensional stability at high temperatures. If the dimension of the sintered article is not held as described above, the micropores can be drastically reduced, or disappear. If a dimension of the porous body in a direction other than the stretching direction is also restricted during this further heat-treatment, the decrease or disappearance of the micropores can be effectively prevented. Such dimensional restriction on the porous body during this heat-treatment can be performed, for example, by holding both extremities of the porous body in its stretching direction with chucks or clips, for example to maintain the distance between the two extremities constant; or by performing the heat-treatment of the porous body between a delivery roll and a take-up roll which are rotating at substantially equal speeds.

This additional heat-treatment is carried out at the temperature at which the porous body will be actually used or higher. Generally, this temperature is 200 to 420°C, preferably 250 to 360°C. In practice, the porous body obtained by the first heating and stretching step is first cooled and then reheated. Alternatively, the porous body is heated immediately following the first heating and stretching step.

The present invention also includes an embodiment in which prior to the first heating and stretching step, the article is pre-stretched at a temperature below the melting point of the PTFE, and during the first heating and stretching step, the article is sintered while it is stretched in the same direction as the direction of the pre-stretching and/or in other directions. When stretching in a direction other than the pre-stretching direction is carried out in this embodiment, the length of the article in its pre-stretching direction is restricted during the performance of the heating and stretching step.

In another embodiment of this invention after the heating and stretching step (when the additional heating step is performed, between this and the additional heating steps), the molded article is again stretched in the same direction as the stretching direction and/or in other directions. If in this embodiment the stretching after the first heating and stretching step is performed in directions other than the stretching direction, the length of the article in the stretching direction of the first heating and stretching step is restricted during the second stretching. If the above dimensional restriction is not performed in this and the former embodiment, the stretched state in the direction in which the dimension is restricted cannot be maintained which is undesirable.

Since two extremities of the article in the direction in which the article is stretched are located outside the heating zone in the present invention, stretching of PTFE articles above the melting point of PTFE, which has heretofore been considered difficult, can be performed in accordance with this invention. In addition, since both sintering and stretching can be performed simultaneously, the number of process steps can be decreased and the resulting porous body has high mechanical strength because it is sintered. The porous sintered product of PTFE can exhibit its function stably over long periods of time, and those porous products which have been subjected to additional heat-treatment have especially high dimensional stability.

The present invention will be explained in greater detail by reference to the following Examples in combination with the accompanying drawings. It should be understood that these Examples in no way restrict the present invention. Unless otherwise indicated, all parts in these Examples are by weight.

#### Example 1

100 parts of PTFE powder (Teflon 6J, a trademark for a product of Mitsui Fluorochemical Co., Ltd.) and 20 parts of naphtha #1 as a liquid lubricant were uniformly mixed. The mixture was compression-molded at a pressure of 20 kg/cm<sup>2</sup>, and then extruded into a rod shape. The rod-shaped product was then passed through a pair of metallic rolls to form a long film-like article having a thickness of 110 microns and a width of 115 mm.

The article was heated at 120°C for 2 minutes. The liquid lubricant was removed, and the article was wrapped around a tubular core in the form of a roll.

Then, as shown in Figure 1, the article 1 wrapped around a tubular core was placed on the unwinding end of a stretching apparatus. One end of the article 1 in its lengthwise direction was led to a take-up roll 2. The temperature of a heating zone was kept at 350°C, and a pair of pinch rolls 4 provided on the inlet side of the heating zone 3 were rotated at a lower speed than a pair of pinch rolls 5 provided on the exit side of the heating zone. Thus, the article 1 was stretched 30% in the lengthwise

direction while sintering that portion of the article which was inside the heating zone 3. Thus, a film-like porous body (Sample No. 1) having a thickness of 108 microns and a width of 93 mm was obtained.

At this time, cold air at 20°C was blown against the pinch rolls 4 and 5 to prevent the softening or melting of base points 6 and 7 for stretching that portion of the molded article 1 which was within the heating zone 3.

The reference numerals 8 and 9 represent guide rolls, and the reference numeral 10, a cooling roll.

Using the article wrapped about a tubular core as above, film-like porous bodies (Sample Nos. 2 to 5) were prepared in the same manner as above except that the stretching ratio and the temperature of the heating zone were varied as shown in Table 1.

The porosities and pore diameters of these porous bodies and their tensile strengths in the stretching direction were measured, and the results are shown in Table 1.

For comparison, the same procedure as in the preparation of Sample No. 2 was performed except that the temperature of the heating zone was set at 300°C. The characteristics for the resulting porous body (Sample No. 6) are also shown in Table 1.

Table 1

Sample No.	Temperature of the Heating Zone (°C)	Stretching Ratio (%)	Porosity (%)	Pore Diameter (μ)	Tensile Strength (kg/mm <sup>2</sup> )
1	350	30	38	0.03—0.9	2.52
2	350	200	62	0.03—2.7	3.97
3	350	550	80	0.03—3.4	4.25
4	380	200	61	0.04—2.9	4.15
5	405	200	60	0.05—3.1	4.09
6	300	200	68	0.01—3.5	1.12

### Example 2

The same article 1 as used in Example 1 was passed through a pair of pinch rolls 4', and led through a heating zone 3' having a progressively increasing width from the inlet side toward the outlet side as shown in Figure 2. The temperature of the heating zone 3' was maintained at 350°C, and the rotating speeds of the pinch rolls 4' and pinch rolls 5' on the outlet side were set substantially equal to each other. Both ends of the article 1 in its width-wise direction were held by chucks of a tenter-type stretching machine 11 provided outwardly of both side ends of the heating zone. With this arrangement, that portion of the molded article 1 which was located within the heating zone was stretched 200% in the widthwise direction to form a film-like porous body (Sample No. 7) having a thickness of 50 microns and a width of 345 mm.

Separately, the article 1 was stretched at a stretching ratio of 200% in the widthwise direction by the tenter-type stretching machine 11 and simultaneously stretched between the pinch rolls 4' and the pinch rolls 5' in the longitudinal direction at a stretching ratio of 200% to afford a biaxially stretched film-like porous body (Sample No. 8).

The characteristics of these porous bodies are shown in Table 2.

For comparison, the same procedures as in the preparation of Sample Nos. 7 and 8 were each repeated except that the temperature of the heating zone was set at 300°C. The characteristics for the resulting Sample Nos. 9 and 10 are also shown in Table 2.

Table 2

Sample No.	Temperature of the Heating Zone (°C)	Stretching Ratio (%)	Porosity (%)	Pore Diameter (μ)	Longitudinal Direction	Widthwise Direction
7	350	200	42	0.03—3.5	3.17	1.88
8	350	each 200	68	0.04—3.8	2.58	1.75
9	300	200	51	0.02—2.3	1.03	0.03
10	300	each 200	77	0.02—2.6	1.25	0.04

### Example 3

The porous body (Sample No. 2) obtained in Example 1 was cut so that its length in the stretching direction became 1 meter. Both ends of the porous body in its stretching direction were held by chucks to restrict its dimension. The porous body was then heat-treated for 10 minutes in a heating oven at 300°C to form a heat-treated porous body (Sample No. 11).

Similarly, the porous body (Sample No. 2) was cut, and heat-treated under the conditions shown in Table 3. Thus, heat-treated porous bodies (Sample Nos. 12 to 14) were obtained.

The porosities of these heat-treated porous bodies were measured. Furthermore, these porous bodies were heated at 200°C for 20 minutes, and the heat-shrinkage and the stretching ratio of each of the samples was calculated in accordance with the following equation. The results are shown in Table 3. Sample Nos. 15 and 16 were comparative samples.

$$\text{Heat Shrinkage (\%)} = \frac{\left( \frac{\text{Dimension before}}{\text{heat shrinkage}} \right) - \left( \frac{\text{Dimension after}}{\text{heat shrinkage}} \right)}{\frac{\text{Dimension before}}{\text{heat shrinkage}}} \times 100$$

The heat-shrinkage of the Sample No. 2 in its stretching direction was 11.9%.

**Table 3**

Sample No.	Dimensional Restriction		Temperature (°C)	Time (min)	Porosity (%)	Heat Shrinkage (%)
	Longitudinal Direction	Widthwise Direction				
11	yes	No	300	10	61	4.8
12	Yes	Yes	300	10	63	5.1
13	Yes	No	350	5	60	2.7
14	Yes	Yes	350	5	61	2.9
15	No	Yes	300	10	50	0.3
16	No	No	300	10	48	0.2

**Example 4**

100 parts of PTFE powder (Teflon 6J, a trademark for a product of Mitsui Fluorochemical Co., Ltd.), 3 parts of azodicarbonamide (Celmik C217, a trademark for a product of Sankyo Kasei K.K., decomposition temperature 215°C) as an azo type foaming agent and 20 parts of fluid paraffin as a liquid lubricant were uniformly mixed. The mixture was compression-molded at a pressure of 20 kg/cm<sup>2</sup>, and then extruded into a rod shape. The rod-shaped product was then passed through a pair of metallic rolls to form a long film-like article having a thickness of 110 microns and a width of 115 mm.

The article was immersed in trichloroethylene to extract and remove the liquid lubricant, and the molded article thus treated was wrapped around a tubular core in a roll form.

Then, the article was processed on the above described apparatus of Figure 1. The temperature of a heating zone was kept at 350°C and the article 1 was stretched 30% in the lengthwise direction while sintering that portion of the article 1 which was inside the heating zone 3. Thus, a film-like porous body (Sample No. 17) having a thickness of 110 microns and a width of 95 mm was obtained.

At this time, cold air at 20°C was blown against the pinch rolls 4 and 5 to prevent the softening or melting of base points 6 and 7 for stretching that portion of the molded article 1 which was within the heating zone 3.

Using the article wrapped about a tubular core as above film-like porous bodies as Sample Nos. 18 to 23 were prepared in the same manner as above except that the stretching ratio and the temperature of the heating zone were varied as shown in Table 4.

The porosities and pore diameters of these porous bodies and their tensile strengths in the stretching direction were measured, and the results are shown in Table 4.

For comparison, the same procedure as in the preparation of Sample No. 2 was performed except that the temperature of the heating zone was set at 300°C. The characteristics for the resulting porous body (Sample No. 24) are also shown in Table 4.

**Table 4**

Sample No.	Temperature of the Heating Zone (°C)	Stretching Ratio (%)	Porosity (%)	Pore Diameter (μ)	Tensile Strength (kg/mm <sup>2</sup> )
17	350	30	40	0.05—2.1	2.56
18	350	200	70	0.08—4.7	3.92
19	350	400	83	0.11—6.8	4.05
20	350	650	87	0.12—7.3	4.17
21	350	900	93	0.14—11.6	4.24
22	380	200	69	0.08—4.7	3.95
23	420	200	68	0.10—5.0	3.12
24	300	200	80	0.03—7.2	1.15

**Example 5**

The same procedures as in the preparation of Sample No. 18 in Example 4 were followed except that 0.5 part and 12 parts of the foaming agent were used to obtain the film-like porous bodies. Sample Nos. 25 and 26, respectively.

5 In addition, the same procedures as in the preparation of Sample No. 18 in Example 4 were followed except that the following foaming agents were used to obtain film-like porous bodies, Sample Nos. 27 to 30. 5

Sample No. 27: p,p'-Oxybisbenzenesulfonyl hydrazide (Celmik S, a product of Sankyo Kasei K.K., decomposition temperature 150°C)

10 Sample No. 28: p-Toluenesulfonyl semicarbazide (Celmik K, a product of Sankyo Kasei K.K., decomposition temperature 135°C) 10

Sample No. 29: N,N'-Dinitrosopentamethylene tetramine (Celmik A, a product of Sankyo Kasei K.K., decomposition temperature 205°C)

Sample No. 30: Ammonium carbonate (decomposition temperature 55°C)

15 The characteristics of these porous bodies are shown in Table 5. 15

For the sake of comparison, the same procedures as in the preparation of Sample No. 25 were followed except that the amount of the foaming agent was 0.05 part. The characteristics of the resulting Sample No. 31 are also shown in Table 5.

20 Further, the same procedures as in the preparation of Sample No. 25 were followed except that the amount of the foaming agent was 20 parts. The moldability of the mixture was poor and a article could not be prepared. 20

**Table 5**

Sample No.	Amount of Foaming Agent (parts)	Porosity (%)	Pore Diameter ( $\mu$ )	Tensile Strength (kg/mm <sup>2</sup> )
25	0.5	68	0.07—4.4	3.77
26	12	73	0.08—6.8	4.05
27	3	69	0.07—4.8	3.84
28	3	69	0.07—4.7	3.75
30	3	70	0.07—4.8	3.72
30	3	68	0.10—8.6	3.56
31	0.05	63	0.02—3.1	4.13

**Example 6**

35 The same article as used in Example 4 (from which the liquid lubricant had removed) was processed in the above-described apparatus of Figure 2. The temperature of the heating zone 3 was maintained at 350°C the rotary speeds of the pinch rolls 4 and the pinch rolls 5 on the outlet side were substantially equal and the stretching machine 11 was used to stretch that portion of the article 1 which was located within the heating zone 200% in the widthwise direction to form a film-like porous body (Sample No. 32) having a thickness of 55 microns and a width of 35 mm. 35

40 Separately, the same article was stretched at a stretching ratio of 200% in the widthwise direction by the tenter-type stretching machine 11 and simultaneously stretched between the pinch rolls 4 and the pinch rolls 5 in the longitudinal direction at a stretching ratio of 200% to afford a biaxially stretched film-like porous body (Sample No. 33). 40

The characteristics of these porous bodies are shown in Table 6.

45 For comparison, the same procedures as in the preparation of Sample Nos. 32 and 33 were each repeated except that the temperature of the heating zone was set at 300°C. The characteristics for the resulting Sample Nos. 34 and 35 are also shown in Table 6. 45

**Table 6**

Sample No.	Temperature of the Heating Zone (°C)	Stretching Ratio (%)	Porosity (%)	Pore Diameter ( $\mu$ )	Tensile Strength (kg/mm <sup>2</sup> )	
					Longitudinal Direction	Widthwise Direction
32	350	200	64	0.08—7.3	3.52	1.68
33	350	each 200	77	0.11—7.7	2.44	1.94
55	300	200	72	0.03—4.2	1.23	0.03
35	300	each 200	85	0.03—4.8	1.15	0.05

**Example 7**

60 The same procedures as in the preparation of Sample No. 17 in Example 4 were followed except that 20 parts of naphtha #1 was used as a liquid lubricant to obtain a long film-like article having a thickness of 55 microns and a width of 35 mm. 60



The article was heated at 120°C for 2 minutes to remove the liquid lubricant. The temperature was increased to 270°C to decompose the foaming agent. After forming numerous micropores in the article, the article was wrapped around a tubular core in a roll form.

5 Thereafter, using the apparatus as shown in Figure 1, the article was sintered and stretched under the conditions shown in Table 7 to obtain film-like porous bodies which were uniaxially stretched in the longitudinal direction and having a thickness of 109 microns and a width of 94 mm (Sample Nos. 36—43).

The characteristics of Sample Nos. 36 to 43 are shown in Table 7.

Table 7

Sample No.	Temperature of the Heating Zone (°C)	Stretching Ratio (%)	Porosity (%)	Pore Diameter (μ)	Tensile Strength (kg/mm <sup>2</sup> )
36	350	30	41	0.05—1.9	2.51
37	350	200	72	0.08—4.5	3.87
38	350	400	85	0.11—6.6	4.02
39	350	650	90	0.12—7.1	4.10
40	350	900	95	0.14—11.4	4.17
41	380	200	70	0.08—4.5	3.88
42	420	200	69	0.10—4.8	3.07
43*	300	200	78	0.03—7.1	1.10

\*Comparison

#### Example 8

The porous body (Sample No. 18) obtained in Example 4 was cut so that its length in the stretching direction became 1 meter. Both ends of the porous body in its stretching direction was held by chucks to restrict its dimension. The porous body was then heat-treated for 10 minutes in a heating oven at 300°C to form a heat-treated porous body (Sample No. 44).

Similarly, the porous body (Sample No. 18) was cut, and heat-treated under the conditions shown in Table 8. Thus, heat-treated porous bodies (Sample Nos. 45 to 47) were obtained.

30 The porosities of these heat-treated porous bodies were measured. Furthermore, these porous bodies were heated at 200°C for 20 minutes, and the heat-shrinkage and the stretching ratio of each of the samples was calculated in accordance with the equation in Example 3. The results are shown in Table 8.

The heat-shrinkage of the Sample No. 18 in its stretching direction was 11.7%.

Table 8

Sample No.	Longitudinal Direction	Widthwise Direction	Temperature (°C)	Time (min)	Porosity (%)	Heat** Shrinkage (%)
44	Yes	No	300	10	69	4.7
45	Yes	Yes	300	10	72	5.0
46	Yes	No	350	5	68	2.5
47	Yes	Yes	350	5	70	2.7
48*	No	Yes	300	10	63	0.3
49*	No	No	300	10	59	0.2

\* Comparison

\*\* Measured as in Example 3.

50 It is seen from the results of the foregoing Examples that the porous PTFE bodies obtained by the process of this invention have high mechanical strength with little variation in the pore diameters of micropores, and that those which were heat-treated have low heat shrinkage and thus superior dimensional stability during use at high temperatures.

#### Claims

1. A process for producing a porous polytetrafluoroethylene body which comprises the steps of, shaping a mixture of a polytetrafluoroethylene powder and a liquid lubricant by extrusion and/or rolling to form an article of the desired shape, disposing the shaped article in a heating zone such that two extremities of the shaped article on an axis in a direction in which the shaped article is to be stretched are located outside the heating zone, heating the portion of the molded article which is within the heating zone at a temperature of the melting point of the polytetrafluoroethylene or higher, and simultaneously stretching the heated molded article in at least one direction.

2. A process as claimed in claim 1, wherein the amount of liquid lubricant is 5 to 50 parts by weight per 100 parts by weight of the polytetrafluoroethylene powder.
3. A process as claimed in claim 1 or 2, wherein said liquid lubricant is a hydrocarbon oil, an aromatic hydrocarbon, an alcohol, a ketone, an ester, a silicone oil, a fluorochlorocarbon oil or a mixture thereof. 5
4. A process as claimed in claim 1, 2 or 3, wherein said liquid lubricant is water or an aqueous solution containing a surface active agent.
5. A process as claimed in any preceding claim, wherein the molded article is a rod, tube or film.
- 10 6. A process as claimed in any preceding claim, wherein said heating is conducted at 340 to 410°C. 10
7. A process as claimed in any preceding claim, wherein said stretching is conducted at a stretching ratio of 10 to 1,000%.
8. A process as claimed in any preceding claim, wherein said porous polytetrafluoroethylene product has a porosity of 35 to 95% and a pore diameter of 0.01 to 100 microns.
- 15 9. A process of claim 1, wherein said mixture further contains a foaming agent. 15
10. A process as claimed in claim 9, wherein the amount of said foaming agent is up to 15 parts by weight per 100 parts by weight of the polytetrafluoroethylene powder.
11. A process as claimed in claim 9 or 10, wherein said foaming agent is an azo-type foaming agent, a hydrazide-type foaming agent, a semicarbazide-type foaming agent or a nitroso type-foaming agent, or a mixture thereof. 20
12. A process as claimed in claim 9, 10 or 11, wherein said foaming agent is ammonium carbonate, sodium bicarbonate or ammonium nitrite or a mixture thereof.
13. A process as claimed in any one of claims 9 to 11, wherein said article containing the foaming agent is pre-heated to at least the decomposition temperature of the foaming agent to decompose the latter. 25
14. A process as claimed in any preceding claim further comprising the step of heat-treating the porous body while maintaining the stretching ratio after the stretching step.
15. A process as claimed in claim 14, wherein said heat-treatment is conducted at the temperature at which the porous body is used or higher.
- 30 16. A process as claimed in claim 14 or 15, wherein said heat-treatment is conducted after cooling the porous body. 30
17. A process as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 8.
- 35 18. A porous polytetrafluoroethylene body when produced by the method as claimed in any preceding claim. 35