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(72) Inventor CHRISTOPHER VALLANCE



(54) POROUS DIAPHRAGMS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of porous diaphragms.

More particularly, the invention relates to the manufacture of porous diaphragms based on polytetrafluoroethylene.

One method of manufacturing such porous diaphragms comprises forming a mixture of an aqueous dispersion of polytetrafluoroethylene and a solid removable particulate filler such as starch, adding an organic coagulating agent such as acetone to said mixture and then drying the coagulated mixture. An organic lubricant such as petroleum ether is then added to the dried coagulated material to serve as a processing aid when the material is being rolled into a sheet. On completion of the rolling operation the starch is removed to give the desired porous diaphragm. The lubricant can also be removed if required.

A major disadvantage of the above method of manufacturing porous diaphragms is that the use of an organic lubricant gives rise to irreproducibility of the diaphragms and this is extremely undesirable particularly when the diaphragms are intended for use in modular electrolytic cells where reproducibility is essential for efficient operation. We have now discovered that the above disadvantage is obviated or mitigated by the method of the present invention in which water is used as lubricant which enables diaphragms of desired reproducibility and permeability to be produced.

According to the present invention a method of manufacturing a porous diaphragm from an aqueous dispersion of particulate polytetrafluoroethylene comprises mixing a solid removable particulate filler into said disper-

sion, thickening the resulting aqueous mixture for the purpose of producing a sheet formable material containing water and having a viscosity of at least 300 poises at 15° C, forming a sheet from said sheet formable material and removing said solid particulate filler from the sheet to render the sheet porous, said sheet formable material containing water alone as lubricant for the sheet forming operation.

In one embodiment of the invention the thickening of the aqueous mixture is effected by reducing the water content thereof to 10% by weight or below.

The desired degree of lubrication for the sheet forming operation preferably is obtained by mixing water with the thickened mixture so that a sheet formable material having a viscosity of at least 300 poises at 15° C is obtained. Preferably, water is added to the thickened mixture so that a sheet formable material having a viscosity of between 1×10^6 and 7×10^6 poises at 15° C is obtained.

Depending on the end use of the diaphragm, the desired degree of lubrication can be achieved either by drying the aqueous mixture to a comparatively low water content and then adding a considerable amount of water to form the sheet formable material or conversely drying the mixture only slightly and adding comparatively less water to form the sheet formable material.

When the diaphragms are intended for use in electrolytic cells the aqueous mixture is preferably dried to a water content of 10% by weight or below.

Further preferably, water is added to the dried mixture until a sheet formable material is attained which has a water content of 20 to 45% by weight.

The drying of the aqueous mixture can be carried out in any suitable manner which will not cause damage to the constituents thereof. Preferably the drying is carried out at a temperature of 10 to 100° C for example 15 to 50° C. The time for drying will depend, inter-

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alia, on the temperature but is generally from 10 to 100 hours, for example, 20 to 50 hours.

5 In a further embodiment of the invention the aqueous mixture is thickened by subjecting it to shearing action at sufficient speed to produce a sheet formable material having a viscosity of at least 300 poises at 15° C, preferably between 1×10^6 and 7×10^6 poises at 15° C.

10 In this embodiment the aqueous mixture advantageously has a water content of 2 to 50%, preferably 20 to 45% by weight.

15 A particularly suitable way of subjecting the aqueous mixture to shear conditions is to treat it in a Z-blade mixer.

When the aqueous mixture is subjected to shear conditions the viscosity increases and shear action is preferably maintained for a time at least sufficient for the viscosity to reach the preferred range.

20 In yet a further embodiment of the invention the aqueous mixture is thickened by first subjecting it to mixing action and then adding a thickening agent to obtain a sheet formable material having a viscosity of at least 300 poises at 15° C.

25 Preferably, the thickening agent is a copolymer of maleic anhydride and an alkyl vinyl ether.

30 The particle size of the polytetrafluoroethylene in the aqueous dispersion is preferably in the range of 0.05 to 1 micron, e.g. 0.1 to 0.2 micron.

35 The solid particulate removable filler can be any which is removed by a suitable chemical or physical means which will not cause damage to the polytetrafluoroethylene. The removable filler may be starch, for example maize starch and/or potato starch, or a water-insoluble inorganic base or carbonate, for example calcium carbonate.

40 These fillers may be removed, for example, by soaking the sheet in an acid, preferably a mineral acid e.g. hydrochloric acid. Other removable fillers which may be used include organic polymers which depending on the properties of the polymer may be removed from the sheet by dissolving with an organic solvent by hydrolysis or by vaporisation.

45 Mixtures of such removable fillers may be used and if necessary various treatments may be given to the sheet to remove the filler.

50 Generally, the removable filler has a particle size substantially all of which are within the range of 5 to 100 microns. The amount of removable filler will depend on the permeability desired in the final diaphragm. Thus, the weight ratio of removable filler to polytetrafluoroethylene may be, for example,

55 from 10:1 to 1:10 preferably from 5:1 to 1:1.

60 In many cases it is desirable to incorporate other components in the aqueous mixture which are not removed when the sheet is subjected to the treatment to remove the solid particulate removable filler. Examples of such

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components include non-removable particulate fillers, generally inorganic fillers, for example, titanium dioxide which is particularly preferred, barium sulphate, asbestos, (e.g. amphibole or serpentine asbestos), graphite and alumina. Suitably the non-removable filler has a particle size of, for example, less than 10 microns and preferably less than 1 micron. The weight ratio of non-removable filler to polytetrafluoroethylene may be for example from 10:1 to 1:10, preferably from 2:1 to 1:2.

70 In some cases it may be advantageous to add a coagulating agent, e.g. brine, to the aqueous mixture to assist in the formation of the sheet formable material.

75 The sheet is generally formed from the sheet formable material by passing the sheet formable material through calender rolls.

80 Generally, after some, or even after every pass through the rolls, the sheets are rotated through 90° so that the calendering is carried out biaxially.

85 The diaphragms produced by the process of the present invention have a wide range of uses but are particularly suitable for use in electrolytic cells for electrolysis of alkali-metal halides, for the production of chlorine and caustic alkalis.

90 They are generally strong enough to be used without any support but for extra strength it may be desirable to incorporate a sheet of a suitable strengthening material, for example, a polymer gauze such as a polypropylene gauze.

95 The process of the present invention enables the production without difficulty of a successive number of diaphragms over a period of time, each one having similar permeabilities. This is very necessary when using the diaphragms in electrolytic cells.

100 The invention is illustrated in the following Examples in which all parts and percentages are by weight.

Example 1.

110 To 100 parts of an aqueous dispersion of polytetrafluoroethylene containing 60% of the polymer in the form of particles approximately all in the size range 0.15 to 0.2 micron were added 101 parts of water, 60 parts of titanium dioxide of particle size approximately 0.2 micron, 60 parts of maize starch of particle size approximately 13 microns and 120 parts of potato starch of particle size less than 75 microns. The aqueous mixture was then stirred with a paddle-mixer for 30 minutes to form a substantially uniform paste. This paste was spread on trays and dried at 24° C for 48 hours to a water content 5.7% by weight. 100 parts of the resultant crumb were mixed with 52 parts of water to form a sheet formable material akin to a dough and having a viscosity of 4×10^6 poise at 15° C. The sheet formable material then

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10 direction of calendaring, into four equal pieces. These were laid congruently over each other to obtain a four layered laminate. The card was picked up, rotated 90° in the horizontal plane, and calendered (directed 90° to the original direction of calendaring) again through the 3 mm roll separation. This process, the successive cutting into four, stacking, rotating and calendaring was repeated until 15 the composition had been rolled a total of five times. The resultant laminate was cut into four, in the direction of calendaring, stacked, removed from the card, and calendered, without rotation through 90°, the inter-roll space being reduced by the thickness of the card. 20 After calendaring, the laminate was cut, at right angles to the direction of calendaring, into four equal pieces, stacked, rotated through 90° and calendered again. This process, cutting at right angles to the direction of calendaring, stacking, rotating and calendaring was repeated until the composition had been rolled a total of nine times. The resultant essentially rectangular laminate was then passed through the rolls with its largest side directed at 90° to the direction of calendaring, and with the inter-roll space slightly reduced, no cutting, stacking or rotating through 90° being involved. This process was repeated through a gradually reduced inter-roll space, the same edge of the laminate being fed to the rolls on each occasion, until the thickness of the laminate was 1.5 mm. 40 A square of 22×26 B.S. mesh gauze woven of 0.011 inch diameter monofilament polypropylene yarn was placed on top of the laminate, and rolled into the laminate by calendaring through a slightly reduced inter-roll space. The resultant reinforced sheet was removed from the rolls and soaked in cold aqueous 18% hydrochloric acid for 24 hours. 45 The starch additive was thereby removed leaving a multi-porous sheet suitable for use as a diaphragm material in electrolytic cells electrolysing aqueous solutions. 50

Example 2.

To 100 parts of an aqueous dispersion of polytetrafluoroethylene containing 60% of the polymer in the form of particles approximately all in the size range 0.15 to 0.2 micron were added 70 parts of water, 60 parts of titanium oxide of particle size approximately 0.2 micron, 60 parts of maize starch of particle size approximately 13 microns and 120 parts of potato starch of particle size less than 75 microns. The mixture was then stirred with a paddle-mixer for 3 minutes to form a paste which was then mixed in a Z-blade mixer for 22 minutes to form

75 der ions, set 5 mm apart, into an oblong sheet. After calendaring, the oblong sheet was cut, in the direction of calendaring, into four equal pieces. These were laid congruently over each other to obtain a four-layered laminate. The card was picked up, rotated 90° in the horizontal plane, and calendered (directed 90° to the original direction of calendaring) again through the 3 mm roll separation. This process, the successive cutting into four, stacking, rotating and calendaring was repeated until the composition had been rolled a total of fifteen times. The resultant laminate was cut into four, in the direction of calendaring, stacked, removed from the card, and calendered, without rotation through 90°, the inter-roll space being reduced by the thickness of the card. After calendaring, the laminate was cut, at right angles to the direction of calendaring, into four equal pieces, stacked, rotated through 90° and calendaring again. This process, cutting at right angles to the direction of calendaring, stacking, rotating and calendaring was repeated until the composition had been rolled a total of nine times. The resultant essentially rectangular laminate was then passed through the rolls with its largest side directed at 90° to the direction of calendaring, and with the inter-roll space slightly reduced, no cutting, stacking or rotating through 90° being involved. 100 This process was repeated through a gradually reduced inter-roll space, the same edge of the laminate being fed to the rolls on each occasion, until the thickness of the laminate was 1.5 mm. A square of 22×26 13.5 mesh gauze woven of 0.011 inch diameter monofilament polypropylene yarn was placed on top of the laminate, and rolled into the laminate by calendaring through a slightly reduced inter-roll space. The resultant reinforced sheet was removed from the rolls and soaked in cold aqueous 18% hydrochloric acid for 24 hours. 110 The starch additive was thereby removed leaving a multi-porous sheet suitable for use as a diaphragm material in electrolytic cells electrolysing aqueous solutions. 115

Example 3.

To 100 parts of an aqueous dispersion of polytetrafluoroethylene containing 60% of the polymer in the form of particles approximately all in the size range 0.15 to 0.2 micron were added 200 parts of water, 60 parts of titanium dioxide of particle size approximately 0.2 micron, 60 parts of maize starch of particle size approximately 13 microns and 120 parts of potato starch of particle size less than 75 microns. The mixture was then stirred with a paddle-mixer for 2 minutes to

gauze woven of 0.011 inch diameter monofilament polypropylene yarn was placed on top of the laminate, and rolled into the laminate by calendaring through a slightly reduced

Permeability tests were conducted on these diaphragms, the results being given in Table I below. Measurements were made with diaphragms installed in an electrolytic cell.

TABLE I

Diaphragm No.	K perm
1	8350
2	840

K perm, (i.e. permeability measured in hrs⁻¹)

flow rate through diaphragm (litres/hour) $\times 10^6$

area of diaphragm (cm²) $\times$ pressure drop (cms, of brine)

In Test Series A the diaphragm was installed in the electrolytic cell and the filler removed by operation of the cell. The permeability of the diaphragm is zero at first, increases as starch is removed and then reduces as the diaphragm becomes blocked during extended operation of the cell. The coefficient of permeability (K perm) is based on measurements taken when the permeability of the diaphragm is at a maximum. Comparison of the permeability factors indicated in Table I for diaphragms produced by identical techniques showed a wide deviation as regards reproducibility.

Test Series B

In this test series a number of diaphragms was prepared according to the process described in Example 1 except that petroleum ether was used as lubricant instead of water. In this case the filler was extracted outside the electrolytic cell by soaking in 16% hydrochloric acid and permeability measurements were made when the diaphragms had been installed in the electrolytic cell. The results are shown in Table II below.

TABLE II

Diaphragm No.	K perm
3	446
4	765
5	492
6	446
7	490
8	253
9	612
10	321
11	262
12	204
13	292
14	959

Mean K perm = 462

Standard Deviation = 226

These results indicate that use of an organic lubricant gives rise to considerable irreproducibility of the diaphragms.

Test Series C

In this series of tests the diaphragms were prepared according to Example 1 with water

being used as lubricant. This time a slightly different technique was adopted in measuring permeability in that a special rig was set up for removal of the filler by acid extraction and the permeability measurements were not made with the diaphragms installed in an electrolytic cell but in said rig. The tests results are indicated in Table III below which also indicates results of tensile strength tests

carried out on the diaphragms on a standard Instron (Registered Trade Mark) tensile strength measuring device. We have established that the tensile strength of a diaphragm is correlated to its permeability and we have found that the tensile strength tests are easier to conduct and the results can be used to accurately predict the permeability of the diaphragm.

TABLE III

Diaphragm No.	K perm $\times 10^3$	Ultimate Tensile Strength (gms mm ⁻²)
15	32	37.2
16	30	40.7
17	20	43.6
18	30	40.0
19	32	39.3
20	32	42.9
21	36	46.0
22	30	37.0
23	28	44.0
24	24	40.0
25	34	40.0
26	34	39.4
27	26	39.2
28	32	49.0
29	20	42.0
30	20	46.0
31	20	45.8
32	20	45.7
33	20	46.0
34	21	47.8

Mean Permeability = 27.1

Mean Ultimate Tensile Strength = 42.6

Standard Deviation = 5.8

Standard Deviation = 3.6

The results listed in Table III indicate that by using water as lubricant diaphragms of desired reproducibility and permeability can be obtained.

5 WHAT WE CLAIM IS:—

1. A method of manufacturing a porous diaphragm from an aqueous dispersion of particulate polytetrafluoroethylene comprising mixing a solid particulate removable filler into said dispersion, thickening the resulting aqueous mixture for the purpose of producing a sheet formable material containing water and having a viscosity of at least 300 poises at 15° C, forming a sheet from said sheet formable material and removing said solid particulate filler from the sheet to render the sheet porous, said sheet formable material containing water alone as lubricant for the sheet forming operation.

20 2. A method as claimed in claim 1 wherein the thickening of the aqueous mixture is effected by reducing the water content thereof to 10% by weight or below.

25 3. A method as claimed in claim 2 wherein the desired degree of lubrication for the sheet forming operation is obtained by mixing water with the thickened mixture until a sheet formable material having a viscosity of at least 300 poises at 15° C is obtained.

30 4. A method as claimed in claim 3 wherein water is added to the thickened mixture until a sheet formable material having a viscosity of between 1×10^6 and 7×10^6 poises at 15° C is obtained.

35 5. A method as claimed in claim 3 or claim 4 wherein water is added to the thickened mixture until a sheet formable material is attained which has a water content of 20 to 45% by weight.

40 6. A method as claimed in any one of claims 2 to 5 wherein the aqueous mixture is dried at a temperature of 10 to 100° C to reduce the water content thereof.

45 7. A method as claimed in claim 6 wherein the drying of the aqueous mixture is carried out at a temperature of 15 to 50° C.

50 8. A method as claimed in any one of claims 2 to 7 wherein the drying of the aqueous mixture is effected over a period of 10 to 100 hours.

9. A method as claimed in claim 8 wherein the drying of the aqueous mixture is effected over a period of 20 to 50 hours.

55 10. A method as claimed in claim 1 wherein the aqueous mixture is thickened by subjecting it to shearing action at sufficient speed to produce a sheet formable material having a viscosity of at least 300 poises at 15° C.

60 11. A method as claimed in claim 10 wherein the viscosity of the sheet formable material obtained is between 1×10^6 and 7×10^6 poises at 15° C.

12. A method as claimed in claim 10 or claim 11 wherein the aqueous mixture has

a water content of 2 to 50% by weight.

13. A method as claimed in claim 12 wherein the aqueous mixture has a water content of 20 to 45% by weight.

14. A method as claimed in any one of claims 10 to 13 wherein the aqueous mixture is subjected to shear conditions in a Z-blade mixer.

15. A method as claimed in claim 1 wherein the aqueous mixture is thickened by first subjecting it to mixing action and then adding a thickening agent to obtain a sheet formable material having a viscosity of at least 300 poises at 15° C.

16. A method as claimed in claim 15 wherein the thickening agent is a copolymer of maleic anhydride and an alkyl vinyl ether.

17. A method as claimed in any one of the preceding claims wherein the particle size of the polytetrafluoroethylene in the aqueous dispersion is in the range of 0.05 to 1 micron.

18. A method as claimed in claim 17 wherein the particle size of the polytetrafluoroethylene is in the range 0.1 to 0.2 microns.

19. A method as claimed in any one of the preceding claims wherein the solid particulate removable filler is removed by chemical or physical means which does not cause damage to the polytetrafluoroethylene.

20. A method as claimed in claim 19 wherein the solid particulate removable filler is starch or a water-insoluble inorganic base or carbonate.

21. A method as claimed in claim 20 wherein the solid particulate removable filler is maize starch and/or potato starch or calcium carbonate.

22. A method as claimed in any one of claims 19 to 21 wherein the solid particulate removable filler is removed by soaking the sheet in acid.

23. A method as claimed in any one of claims 1 to 19 wherein the solid particulate removable filler is an organic polymer removable by dissolving the sheet in an organic solvent or by hydrolysis or by vaporisation.

24. A method as claimed in any one of the preceding claims wherein the solid particulate removable filler has a particle size substantially within the range 5 to 100 microns.

25. A method as claimed in any one of the preceding claims wherein the weight ratio of solid particulate removable filler to polytetrafluoroethylene is 10:1 to 1:10.

26. A method as claimed in claim 25 wherein the weight ratio of solid particulate removable filler to polytetrafluoroethylene is 5:1 to 1:1.

27. A method as claimed in any one of the preceding claims wherein the aqueous mixture comprises other components which are not removed when the sheet is subjected to the treatment to remove the solid particulate removable filler.

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The results listed in Table III indicate that by using water as lubricant diaphragms of desired reproducibility and permeability can be obtained.

5 WHAT WE CLAIM IS:—

- 10 1. A method of manufacturing a porous diaphragm from an aqueous dispersion of particulate polytetrafluoroethylene comprising mixing a solid particulate removable filler into said dispersion, thickening the resulting aqueous mixture for the purpose of producing a sheet formable material containing water and having a viscosity of at least 300 poises at 15° C, forming a sheet from said sheet formable material and removing said solid particulate filler from the sheet to render the sheet porous, said sheet formable material containing water alone as lubricant for the sheet forming operation.
- 15 2. A method as claimed in claim 1 wherein the thickening of the aqueous mixture is effected by reducing the water content thereof to 10% by weight or below.
- 20 3. A method as claimed in claim 2 wherein the desired degree of lubrication for the sheet forming operation is obtained by mixing water with the thickened mixture until a sheet formable material having a viscosity of at least 300 poises at 15° C is obtained.
- 25 4. A method as claimed in claim 3 wherein water is added to the thickened mixture until a sheet formable material having a viscosity of between 1×10^6 and 7×10^6 poises at 15° C is obtained.
- 30 5. A method as claimed in claim 3 or claim 4 wherein water is added to the thickened mixture until a sheet formable material is attained which has a water content of 20 to 45% by weight.
- 35 6. A method as claimed in any one of claims 2 to 5 wherein the aqueous mixture is dried at a temperature of 10 to 100° C to reduce the water content thereof.
- 40 7. A method as claimed in claim 6 wherein the drying of the aqueous mixture is carried out at a temperature of 15 to 50° C.
- 45 8. A method as claimed in any one of claims 2 to 7 wherein the drying of the aqueous mixture is effected over a period of 10 to 100 hours.
- 50 9. A method as claimed in claim 8 wherein the drying of the aqueous mixture is effected over a period of 20 to 50 hours.
- 55 10. A method as claimed in claim 1 wherein the aqueous mixture is thickened by subjecting it to shearing action at sufficient speed to produce a sheet formable material having a viscosity of at least 300 poises at 15° C.
- 60 11. A method as claimed in claim 10 wherein the viscosity of the sheet formable material obtained is between 1×10^6 and 7×10^6 poises at 15° C.
12. A method as claimed in claim 10 or claim 11 wherein the aqueous mixture has

a water content of 2 to 50% by weight.

13. A method as claimed in claim 12 wherein the aqueous mixture has a water content of 20 to 45% by weight.

14. A method as claimed in any one of claims 10 to 13 wherein the aqueous mixture is subjected to shear conditions in a Z-blade mixer.

15. A method as claimed in claim 1 wherein the aqueous mixture is thickened by first subjecting it to mixing action and then adding a thickening agent to obtain a sheet formable material having a viscosity of at least 300 poises at 15° C.

16. A method as claimed in claim 15 wherein the thickening agent is a copolymer of maleic anhydride and an alkyl vinyl ether.

17. A method as claimed in any one of the preceding claims wherein the particle size of the polytetrafluoroethylene in the aqueous dispersion is in the range of 0.05 to 1 micron.

18. A method as claimed in claim 17 wherein the particle size of the polytetrafluoroethylene is in the range 0.1 to 0.2 microns.

19. A method as claimed in any one of the preceding claims wherein the solid particulate removable filler is removed by chemical or physical means which does not cause damage to the polytetrafluoroethylene.

20. A method as claimed in claim 19 wherein the solid particulate removable filler is starch or a water-insoluble inorganic base or carbonate.

21. A method as claimed in claim 20 wherein the solid particulate removable filler is maize starch and/or potato starch or calcium carbonate.

22. A method as claimed in any one of claims 19 to 21 wherein the solid particulate removable filler is removed by soaking the sheet in acid.

23. A method as claimed in any one of claims 1 to 19 wherein the solid particulate removable filler is an organic polymer removable by dissolving the sheet in an organic solvent or by hydrolysis or by vaporisation.

24. A method as claimed in any one of the preceding claims wherein the solid particulate removable filler has a particle size substantially within the range 5 to 100 microns.

25. A method as claimed in any one of the preceding claims wherein the weight ratio of solid particulate removable filler to polytetrafluoroethylene is 10:1 to 1:10.

26. A method as claimed in claim 25 wherein the weight ratio of solid particulate removable filler to polytetrafluoroethylene is 5:1 to 1:1.

27. A method as claimed in any one of the preceding claims wherein the aqueous mixture comprises other components which are not removed when the sheet is subjected to the treatment to remove the solid particulate removable filler.



28. A method as claimed in claim 27 wherein said other component is a non-removable inorganic filler.
- 5 29. A method as claimed in claim 28 wherein the inorganic filler is titanium dioxide, barium sulphate, asbestos, graphite or alumina.
- 10 30. A method as claimed in any one of claims 27 to 29 wherein said other component has a particle size less than 10 microns.
31. A method as claimed in claim 30 wherein said other component has a particle size less than 1 micron.
- 15 32. A method as claimed in any one of claims 27 to 31 wherein the weight ratio of said other component to polytetrafluoroethylene is 10:1 to 1:10.
33. A method as claimed in claim 32 wherein said weight ratio is 2:1 to 1:2.
- 20 34. A method as claimed in any one of the preceding claims wherein a coagulant is added to the aqueous mixture.
35. A method as claimed in claim 34 wherein the coagulant is brine.
- 25 36. A method as claimed in any one of the preceding claims wherein the sheet is formed by passing the sheet formable material through calender rolls.
37. A method as claimed in claim 36 wherein after some or after every pass through the rolls, the sheet is rotated through 90° so that the calendering is carried out biaxially.
- 30 38. A method as claimed in any one of the preceding claims wherein the diaphragm is provided with a strengthening support.
- 35 39. A method as claimed in claim 38 wherein the support is a sheet of polymer gauze.
40. A method as claimed in claim 39 wherein the support is a polypropylene gauze.
- 40 41. A method of manufacturing a porous diaphragm according to claim 1 and substantially as hereinbefore described with reference to the Examples.
- 45 42. A porous diaphragm whenever prepared by any of the methods of claims 1 to 41.
43. An electrolytic cell fitted with the diaphragm of claim 42.

A. McPHERSON,
Agent for the Applicants.