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THE MEASUREMENT OF MEMBRANE FILTER PORE SIZE BY A GAS PERMEABILITY TECHNIQUE

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SUMMARY

A differential low pressure gas flow technique has been developed for the measurement of the mean pore size of membrane filters. The method is here applied to the pore size determination in a range of commercial microporous polymer films with pore diameters ranging from 0.03 to 0.8 μm ('Nuclepore'). The polymer films were also examined using scanning electron microscopy so that structural and physical parameters could be evaluated. Two flow regimes could be demonstrated for the permeability data with clear separation between diffusional (Knudsen) flow and viscous or transitional flow occurring at a pore size of 0.2 μm. Alternative theoretical treatments are required for the two regimes but mean pore diameters could be calculated with reasonable precision and agreed with the results obtained by microscopy. In the case of viscous flow it is necessary to assume that the membranes have a tortuosity of less than unity and this is shown to be justified from a consideration of the structure of the pore in the plastic film.

INTRODUCTION

During our current investigation into the physical properties of tablets and coatings[1,2] it has become necessary to determine the mean pore size of the compacted powders used in our studies. The measurement of gas permeability through a porous medium is a convenient method of characterising the otherwise complex geometry and properties of pore spaces within the medium. We were also impressed by the close parallels between the filtration process and the penetration of liquids into powder compacts. For this reason we felt that the evaluation of a device for measuring tablet pore size could be profitably undertaken by comparing the pore sizes of filters with those measured by a reference method.

The theoretical background for the flow of gases through porous membranes has been discussed by Carman[3] and Barrer[4] and applied to Millipore filters by others.[5,6] These filters have a three dimensional porous structure which is less than easy to relate to the results obtained by permeability methods and the 'Nuclepore' filters appeared, at least at first sight, to have a number of attractions. These materials are prepared by exposing sheets of polycarbonate to uranium metal in a nuclear reactor. Fission tracks in the plastic can be etched out by an alkaline washing process. The number of pores in a given area is controlled by the exposure time in the reactor and the size of the pore by the duration of the etching process so that, in theory at least, this type of filter is likely to be more absolute in its structure and behaviour than the other types of membrane filter.[8,9] Stamm,[10] for

example, has demonstrated that Nuclepore filters are more uniform than the cellulose acetate membranes.

Barrer and Grove[11] pointed out that the flow of gases through porous media is similar to flow through single capillaries in that there is turbulent flow, streamline or viscous flow and molecular streaming diffusional or Knudsen flow. These authors showed that there were advantages in investigating pore properties in regions where molecular streaming was likely to occur, i.e. in regions where the mean free path of the gas molecules was much greater than the dimensions of the pores through which the gas is permeating. Molecular streaming may be induced by operating at low pressures. Empirically, in initial experimental work, it was found that there should only be a small differential pressure on the compact or filter which otherwise could become subject to distortion or other physical alteration. In addition, although an attempt was made to determine pore size from the transient flow data by using the time for a steady state to be initiated[12,13] this was found to be irreproducible. Accordingly a device was built which enabled the rate of permeation to be determined under steady state conditions.

EXPERIMENTAL

Materials - 'Nuclepore' filters (Nuclepore Corporation, California) obtained as samples from Shandon Southern Instruments Ltd., Camberley, Surrey, U.K., with nominal pore diameters of 0.03, 0.05, 0.08, 0.1, 0.2, 0.4, 0.6 and 0.8 μm. Nitrogen and helium compressed from

cylinders, British Oxygen Company and air, all dried by passage through a bed of silica gel followed by another of phosphorous pentoxide.

Apparatus - The low pressure gas permeability apparatus is shown diagrammatically in Fig.1. It consists of two steel pressure vessels, A and B, 0.5 dcm^3 capacity and either side of a sample holder C. The filter sample is held between the two halves of the holder by means of neoprene O-rings against a face machined flat and smeared with vacuum grease. After filling with the appropriate dry gas through inlet H the apparatus is evacuated with a Gallenkamp rotary vacuum pump, the tap D being closed to vessel A. When the vacuum reaches 4 Pa (0.03 Torr) gas is admitted from vessel A to the required initial pressure through tap D and the pressure decline to that of the downstream side (Maintained at 4 Pa) monitored by means of the Edwards Pirani gauge Model 12(F) connected to the chart recorder G. The membrane permeability coefficients were determined from the linear portions of the pressure/time curve. The pressure vessels and the permeability cell were housed in an air thermostated cabinet maintained at $25^{\circ} \pm 1$.

Scanning microscopy-Filters from the same batches as those examined above were vacuum coated with gold and examined at 15 or 25 KV using a JEOL JSM Model 50A electron scanning microscope. Photographs of selected fields were taken and the pore frequency and size determined, measuring at least 150 pores.

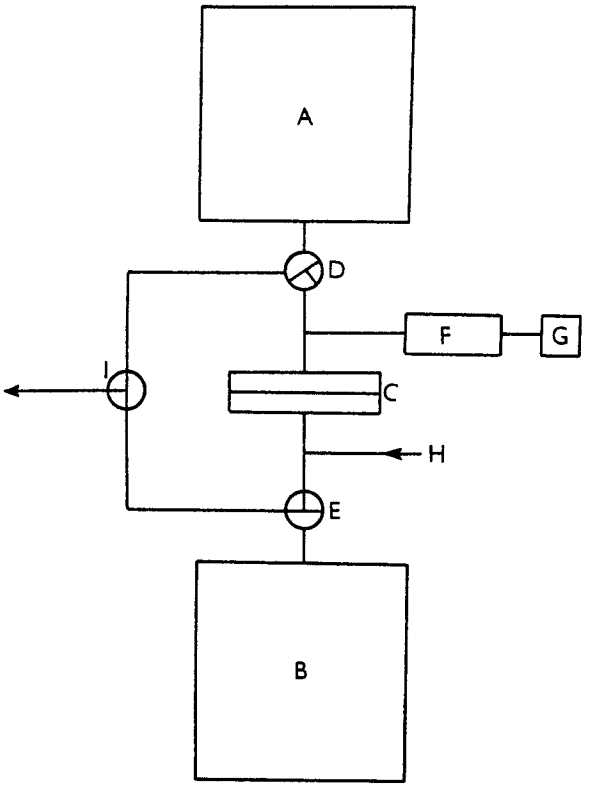

FIGURE 1

Diagrammatic section of Low Pressure Permeability Apparatus.

A and B	pressure vessels, 0.5 dcm^3 capcity.
C	sample holder
D and E	three-way taps
F	Pirani gauge
G	chart recorder
H	gas inlet
I	tap to vacuum pump

Theory

The gas flux J through a membrane of thickness L can be generally expressed by $J = K.\Delta p/L$, where Δp is the pressure difference between the upper and lower surfaces and K is the proportionality factor or permeability coefficient. It has been shown[3,6] that K is made up of two components, the first being due to the molecular streaming or Knudsen flow, Ko, and the second due to the viscous flow, so that it is possible to write $K = Ko + (Bo/\eta).\bar{p}$, where Bo is the geometric factor of the membrane, η is the viscosity of the permeating gas and $\bar{p}$ is the mean pressure across the membrane. A plot of the permeability coefficient against $\bar{p}$ gives a straight line of slope (Bo/η) and intercept Ko.

The Knudsen permeability coefficient may be written[11] as

$$Ko = 4/3.e.r.\ \delta_o/k_1.\ (2RT/\pi M)^{\frac{1}{2}}$$

where e = porosity $(= N\pi r^2)$, r = pore radius, δ_o = fraction of diffuse inelastic collisions between the diffusing molecules and the pore walls (assumed to be unity[3]), k_1 = Knudsen flow shape factor (also assumed to be unity[3]), R = Gas Constant, T = absolute temperature, M = molecular weight of the gas permeating, N = the number of parallel cylindrical capillaries, m^{-2}.

The geometric factor Bo is a specific property of the porous medium under conditions of viscous flow and is generally expressed[3] as

$Bo = er^2/(4\ koq^2)$, where ko is a shape factor introduced for viscous flow and assigned a value of 2, and q is the tortuosity factor.

Combination of these equations allows an expression for the pore diameter D to be obtained $D = 2r = 64/3\ (Bo/Ko)q^2.\ (2RT/\pi M)^{\frac{1}{2}}$.

RESULTS

The permeability coefficients for the different filters are shown in Fig. 2 as a function of the inlet pressure of nitrogen under steady state conditions and it can be readily appreciated that for filters with nominal pore sizes below 0.2 μm the viscous flow element is either very small or non-existent. The separation of the results into two clearly defined groups is also due, in part, to the fact that the smaller pore sizes of membrane are thinner, being only 5 μm thick as opposed to 10 μm and the effect is to decrease the value of the permeability coefficient overall.

Experimental results obtained by permeability and electron microscopy are compared in Table 1. Results obtained on the 0.05 μm nominal pore size filter for different gases are shown in Table 2.

It should be noted that for the coarser filters, where there is viscous flow, it is necessary to assume a tortuosity of 0.5 in order to obtain the results shown in Table 1.

DISCUSSION

Since the object of the exercise was to evaluate the apparatus and gain experience on the measurement of a mean pore size, the results obtained in

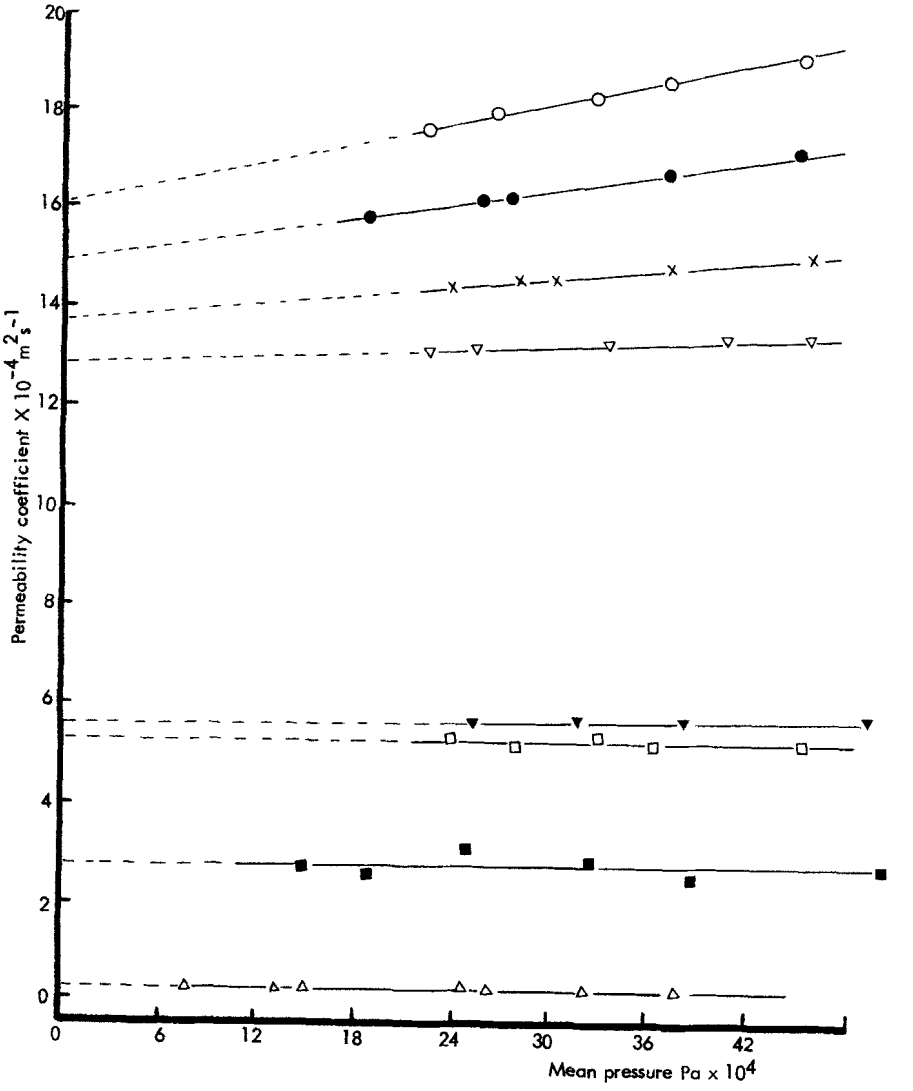

FIGURE 2.

Permeability Coefficients Measured at Different Mean Pressures Using Nitrogen at 25°.

Key:

'Nuclepore' membranes nominal pore size

○	0.8 μm	×	0.4 μm	▼	0.1 μm	■	0.05 μm
●	0.6 μm	▽	0.2 μm	□	0.08 μm	△	0.03 μm

TABLE 1.

The Mean Pore Size of 'Nuclepore' Membrane Filters Obtained by Different Methods

Manufacturers nominal pore size (μm)	Nos. of pores/m^2 by microscopy (N) X10^{11}	Thickness (L) μm	Intercept Ko $m^2 s^{-1} \times 10^{-7}$	Slope Bo/η (correlation coefficient)	Pore diameter / permeability Nitrogen at 25°	μm / S.E.M.
0.03	52.96	5	0.198	-	0.031	0.033
0.05	69.70	5	2.74	-	0.068	0.061
0.08	74.21	5	5.26	-	0.083	0.081
0.10	31.80	5	5.64	-	0.113	0.097
0.20	24.60	10	12.81	1.20 (0.998)	0.207 *	0.175
0.40	5.11	10	13.75	2.57 (0.982)	0.414 *	0.410
0.60	2.52	10	15.05	4.01 (0.996)	0.589 *	0.607
0.80	2.08	10	16.15	5.95 (0.997)	0.816 *	0.801

* calculated by assuming q = 0.5

TABLE 2.

Pore Sizes Obtained by Permeating Different Gases Through a Nominal 0.05 μm filter

Gas	Ko $m^2s^{-1} \times 10^{-7}$	Pore diameter (μm)
helium	5.61	0.063
nitrogen	2.74	0.068
air	2.44	0.066

Table 1 would appear to be satisfactory, suggesting that the method is capable of allowing a mean to be calculated from low pressure permeability data. Experience has shown that the manufacturers nominal pore size, claimed to be approximately 10% less than the maximum, may not always be realistic although -there is broad agreement here between the S.E.M. and the permeability results. Examples of these filters (not reported here) have been seen in which there are either a very small number of pores through the membrane or, alternatively, there is an excessive number of overlapping pores, giving either appreciably smaller or larger mean values.

The very clear separation of flow regimes shown in Fig.2 into those showing viscous together with diffusional flow or diffusional flow alone is of interest and can be contrasted with the data obtained by Yasuda and Tsai[6] who found only the former type of behaviour for Millipore and

polysulphone membranes over approximately the same size range. However, these workers were using a high pressure technique such that the low pressure side of the membrane was held constant at atmospheric pressure. Under these conditions it would be anticipated that the viscous forces involved would be considerably larger than those in the present work where the gas molecules have a mean free path more comparable in dimensions to those of the pores so that diffusional forces are operative. Under Knudsen Flow conditions, it will be noted that there is a linear relationship between the value of Ko and the product of the porosity ($N\eta r^2$) and the pore radius, i.e. $Ko \propto Nr^3$. This relationship is plotted in Fig.3

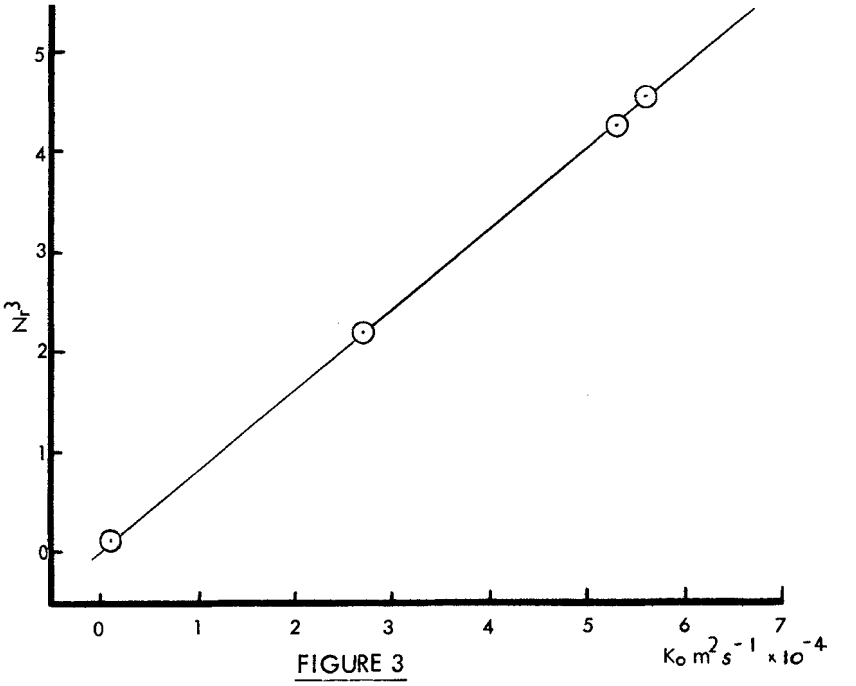

FIGURE 3

Knudsen Flow Component of Nitrogen Flow Through the Smaller 'Nuclepore' Membranes vs. the Product of the Porosity and Pore Radius.

taking the value of r from the S.E.M. experiments and is seen to deviate very strongly once the pore size exceeds 0.10 μm. Similarly, taking into account viscous flow, a plot of Bo/Ko vs pore size, Fig. 4, is also linear,

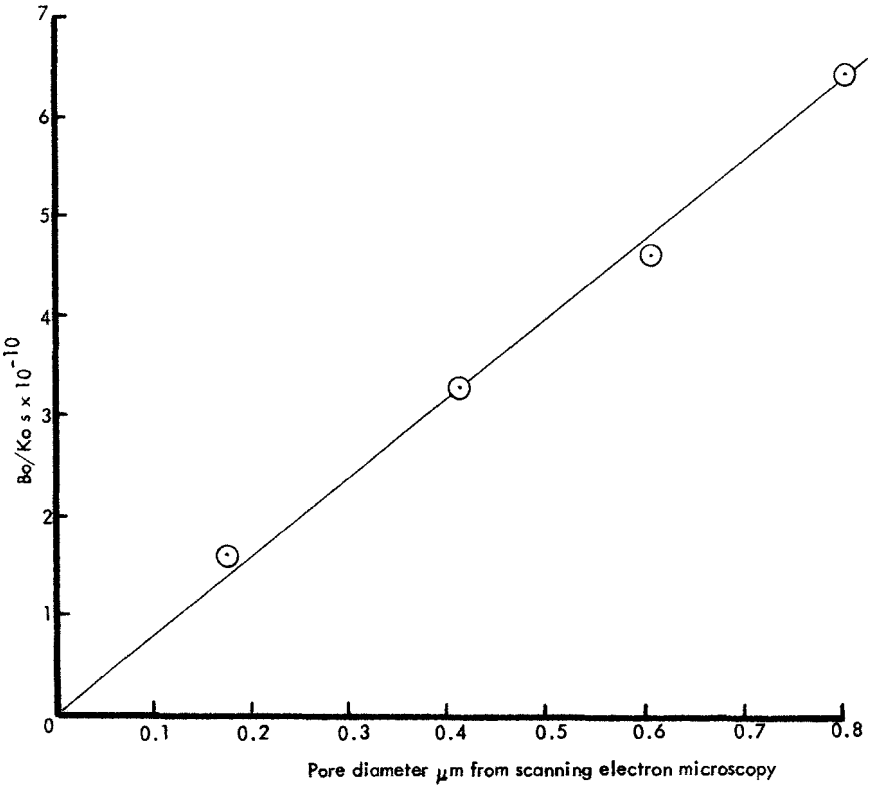

FIGURE 4

The Viscous Flow Component For the Flow of Nitrogen Through the Larger 'Nuclepore' Membranes as a Function of the Pore Diameter.

passing through the origin, for the larger pores, and both plots tend to confirm the underlying suppositions of two quite separate flow regimes.

However, from the morphological point of view, the necessity of having to employ a tortuosity factor of less than unity for the viscous flow was surprising and requires comment. In theory at least, and according to the manufacturers, the pores should be straight-through cylinders, a tortuosity of unity. In fact this is not the true situation since the two surfaces of the membranes are not equivalent. This may be seen visually since one surface is smooth and the other dull in appearance. When examined on the S.E.M., Fig.5 and 6, a marked difference could be demonstrated, the dull surface showing that the regular pores on one surface tend to become confluent on the other. This effect was more pronounced for the thicker membranes, coincidentally those which demonstrate viscous flow. The same effect can be seen in photomicrographs published by Fleischer and others.[8,9] It would appear that the neutron tracks in the polycarbonate are more or less linear and normal to the surface for the first approximately 5 μm, after which they tend to deviate in different directions so that they are able to join up in an irregular fashion. At this point the pores obviously become much larger and irregular, forming pits on the dull or exit surface. Attempts to measure the depth of the pits were not successful but if the assumption is made that the depth of regular

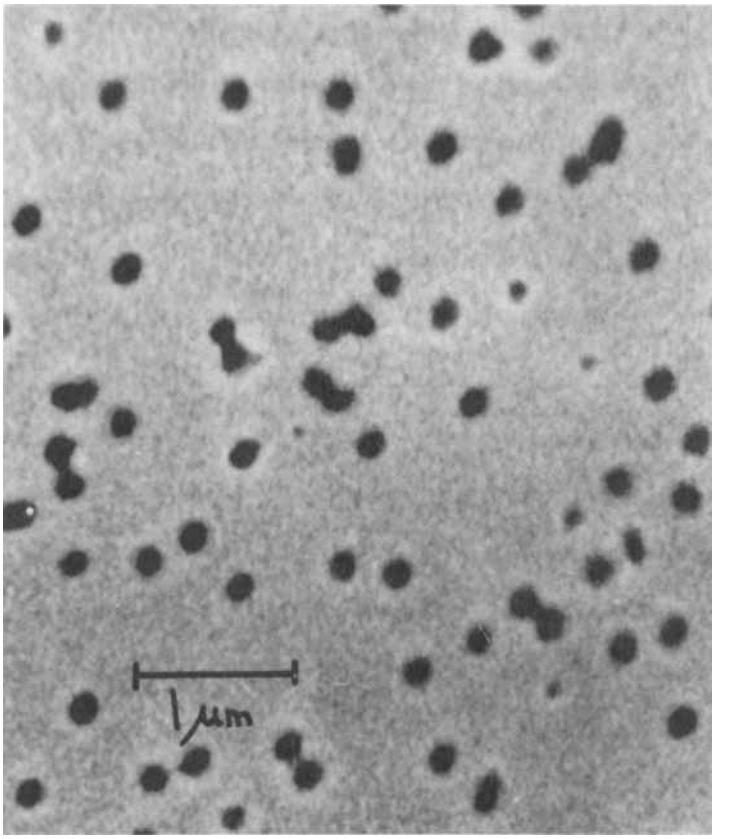

FIGURE 5

Scanning Electron Photomicrograph of the Smooth (Upper) Surface of a 0.2 µm Nominal Nuclepore Membrane (bar = 1 µm).

separated pores is approximately 5 µm the tortuosity becomes approximately 0.5. Assigning this value to the viscous flow term in the equation gives the values obtained in Table 1 which would appear to be in quite reason-

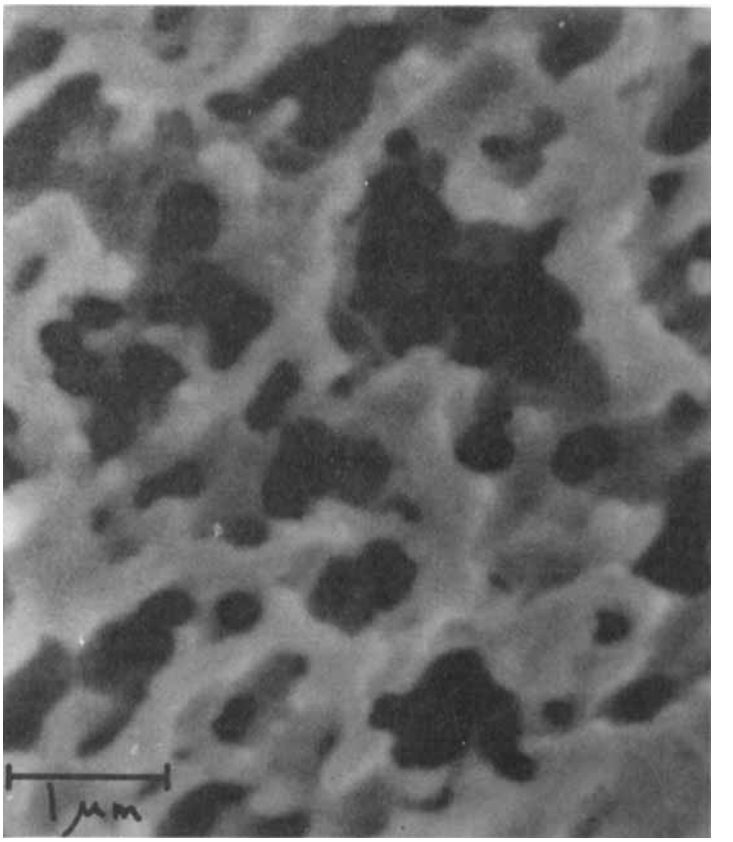

FIGURE 6

Scanning Electron Photomicrograph of Dull (Lower) Surface of Same Membrane Shown in Figure 5 (bar = 1 µm)

able agreement with the values obtained by S.E.M. for the pore sizes on the shiny surfaces.

It may be concluded that this low pressure differential permeability method is capable of providing a measurement of the mean pore size of a

membrane. When applied to a tablet or powder compact the porosity term may be obtained from the dimensions of the compact. The problem of assigning a value for the tortuosity does not affect the theoretical treatment provided that the pressure is sufficiently low to ensure that the Knudsen flow regime is predominant.

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