CRI NUMBER → '75 8320

R & D REPORT

DOW CHEMICAL U.S.A.

RESTRICTED: for use within The Dow Chemical Company only.

CRI NUMBER: 75 8320
LABORATORY REPORT CODE: LAD-347
DATE ISSUED: October 17, 1975
DEPARTMENT: RESEARCH AND DEVELOPMENT
LAB. NO.: 274
PROBLEM NO.:

TITLE: CHLORINE CELL NON-ASBESTOS DIAPHRAGMS, PART 1

18 PAGES IN FULL REPORT

PLAINTIFF'S EXHIBIT
DOW-717

AUTHOR (S): Carlos M. Moreno
AUTHOR (S) SIGNATURE (S): Carlos M Moreno
REVIEWER'S SIGNATURE: R. O. Bridges

This report is: [X] INTERIM [ ] FINAL and mainly: [ ] NEW [X] REVIEW

DESCRIPTIVE SUMMARY WITH CONCLUSIONS: (Include in this space references to data books, and to earlier related reports, patents and publications.)

SUMMARY

The theory of porous plastics membranes in its connection to chlorine cell diaphragms is reviewed and related to math modeling with emphasis on the requisites for a membrane to act as a chlorine cell diaphragm.

This is the first of a series of reports on porous plastics diaphragms.

ST0284935

CONCLUSIONS

The anticipated characteristics for a chlorine cell diaphragm are -

- solvent permeable membrane
- high void content (> 70% porosity)
- pore sizes in the order of magnitude of 1-10 microns
- thicknesses in the order of magnitude of 10 to 100 mils

Characterization of a plastic diaphragm should include -

- chemical nature
- microcristalline structure
- pore statistics
- cell type
- degree of asimetry
- permeability
- resistance to compaction
- temperature stability

The most important mechanical properties are -

- resistance to cold flow with collapsing of the smaller pores and enlargement of the larger ones
- stiffness, determining whether the material can be formed into shapes or not

Morphology is largely set by the fabrication technique

DISTRIBUTION: DEPARTMENT FILES
R & D ADMINISTRATION
CENTRAL REPORT INDEX - 5 COPIES (566 Bldg. - Midland)

Distribution list is continued on attached page.

FORM C-4300 PRINTED R-1-73

INTRODUCTION

This is the first of a series of reports on the development of porous plastics diaphragms. It covers the theory and background on which further research is based. Besides serving as an introduction for the rest of the reports, the material covered here attempts to provide a review of the state of the art at the present time and the basis for a better understanding of the path followed in the development of a porous plastic diaphragm.

The material presented here comprises membrane theory and structure and the results of math modeling.

ST0284936

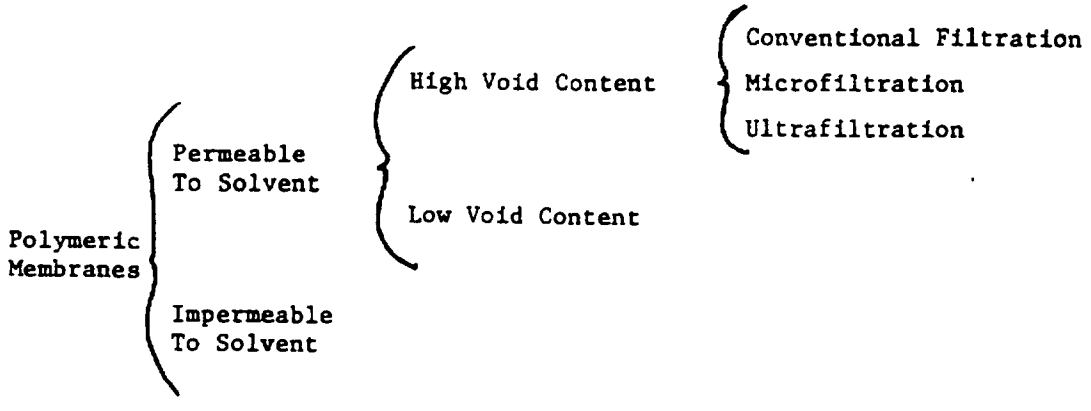
THEORY

Porous Membranes

This section attempts to summarize the most important characteristics of microporous membranes in connection with their application to chlorine cell technology to provide a better understanding of the next reports of this series in their correlation of structural characteristics to performance.

The discussion will be restricted to microfiltration membranes, their structure and fabrication with exclusion of other membrane types (ion exchange, reverse osmosis) that can also be used in a chlorine cell but that will require a drastic change in the process, or cell design. Therefore, only membranes that can replace asbestos diaphragms with little change from present technology, will be considered.

Classification of Membranes - Although different criteria can be used to classify synthetic membranes, it is suitable for our purposes to divide them as follows:



We are only interested here in membranes permeable to solvents and of high void content; these two constraints arising from the fact that a bulk flow of brine should exist across the diaphragm and that the electrical resistance should be as low as possible.

These requirements place us in the field of filtration. The third requirement for a chlorine cell diaphragm is given by the hydraulic characteristics - a suitable diaphragm for the existing Dow chlorine cells is required to have a permeability of approximately 0.2 gallons per hour per square foot at heads between 1 and 2 feet of brine.

REVIEW OF MATH MODEL

A previous math model (1) showed that a series of combinations of porosity, thicknesses and pore sizes would operate satisfactorily as chlorine cell diaphragms. Of these combinations, only a limited range is practically feasible.

It was found desirable to maintain the porosity as high as possible to reduce the voltage drop across the diaphragm. The practical upper limit is between 70 and 85% void space for the material to have enough physical strength and integrity. In this range, the thickness of the material forming the walls of the pores is much smaller than the diameter of the pores at these high porosities. The hydraulic characteristics require pore sizes of the order of magnitude of 1 micron (1 to 10 microns) although, probably actual materials will tend to deviate from the results of the math model according to their pore size distribution.

These two previous constraints fix the thicknesses of the diaphragms predicted by the math model between 5 and 200 mils and most likely between 10 and 100 mils.

In summary, the basic requirements for a chlorine cell diaphragm are -

1. solvent permeable membrane
2. high void content (60 to 85% porosity)
3. pore sizes in the order of 1 to 10 microns

A closer look at the micron rating reveals that we are in the upper edge of ultrafiltration membranes, in the 50% range of microfilters of just in the lower limit of conventional filtration. This is illustrated in Figure 1 where the range of each application is plotted against particle sizes, based on the assumption that pore and particle sizes correspond.

In order to dramatize this point, Figure 2 shows (shaded area) the most common industrial mists and dusts with particle sizes in the same order of magnitude (1 to 10 microns).

ST0284937

A more specific characterization of the membranes in the range of interest will include -

1. chemical nature
2. microcristalline structure
3. pore statistics
4. cell type
5. degree of asimetry
6. permeability
7. resistance to compaction
8. temperature stability

1. Chemical Nature - The first aspect is the chemical resistance of the material itself in the chlorine cell environment: the polymeric material should be completely inert. Only Teflon and Kynar membranes have been found to be stable when functioning as chlorine cell diaphragms (1) other chlorinated and/or fluorinated polymers seem to be appropriate also, but we do not know of any currently available porous sheets made of them. It is interesting to point out here that the chemical attack may occur in two ways: a) the polymeric material is dissolved and the weight of the diaphragm decreases with time and b) the polymeric material becomes chlorinated, in this case, the diaphragm tends to become extremely brittle, cracks occur or the sheet is reduced to power. A phenomenon related to chlorinattion (and in some cases hydrolysis in either acid or basic media) is the collapsing of the polymer conglomerates (christalline or amorfous structure) leading to the disintegration of the structure.

   The second aspect is the hydrophobic/hydrophilic nature of the polymer that can be detected by the wettability, permeability and/or swelling of the membranes. Polar macromolecules such as polytetrafluoroethilene will have a tendency to be strongly hydrophobic repelling the water clusters, known to be formed by about 100 hydrogen bonded molecules, each molecule with four to six nearest neighbors. Introduction of SO_3H - CH, NH_2, and OH groups may increase the wettability of the polymer. This can be done by modifying the polymer itself, like in DuPont's Nafion membrane, (itself an ion exchange membrane) when fabricated as a porous material, or by surface grafting, in which case the grafted material tends to be washed-out(unless strongly bonded to the substrate) after several weeks of operation. Rather permanent graphs on Teflon membranes have been claimed by various manufacturers. They also have some permselectivity properties.

(1) Diaphragms made out of polyethylene and polypropylene have also been reported in the literature.

ST0284938

2. Crystallinity - Most reports on crystallinity of porous membranes found in the literature are in connection with dense membranes and gas permeation. In our case, we are rather interested in crystallinity as related to pore structure and cold flow. Crystallinity is important on one side to maintain the highly porous, sponge-like structure, and durability of the membranes may depend on the crystallization of the raw material and method of fabrication used, and on the other side, to maintain the pore size distribution, preventing small pores to collapse and large pores to become larger when the membrane is subjected to changes in temperature or pressure or even local stresses.

   Although the structural integrity of the membrane can be related to crystallinity (by x-ray diffraction) this aspect, to the present, has been left as one of the specifications to the manufacturers, which are required to furnish membranes that do not change in physical properties with time under operating conditions and has not been included within the scope of this project.

3. Mechanical Properties - The most important mechanical properties are compression and stiffness. The first one is important in order that the void space in the membrane does not change with the head applied, causing an increase in voltage, and failing to produce the desired increase in flow. A small increase in voltage with head has been observed in some Teflon membranes, but correlation to compression is not evident. Kynar membranes, in general, do not exhibit such behavior, and are in turn more rigid than Teflon membranes that have a chamois-like texture. This is a factor in the fabrication of diaphragms of chlorine cells - Teflon membranes can be easily stretched and fitted, while Kynar membranes require forming by the manufacturer and are more likely to tear during handling.

4. Pore Statistics - It appears that the most desirable membrane is one with a very narrow pore size distribution. However, only nuclepore asimetric membranes can be obtained with a very precise controlled pore size (see below). Most manufacturers classify membranes pore rating according to the following criteria -

   1) size of the largest particle passing through the membrane
   2) average pore size
   3) 95% of the pores under a specific value

   These different criteria have led in the past to confusing the specification of pore ratings. In particular, when the average pore size is quoted, the spread of the distribution can change from manufacturer to manufacturer. However, we found that for a particular material, this is the most useful criterium, adding that the distribution should be as narrow as possible. In most cases, the distribution is not symmetrical and will have a form like in Figure 3 (for a typical Kynar membrane).

ST0284039

Math modeling may also help to predict the optimum shape of the pres. Although this is not a direct conclution from the results obtained (1) the form of the equations seem to indicate that the sectional area of the pores should be inversely proportional to the concentration gradient at any point in the diaphragm, suggesting a nozzle-like pore with the throat facing the anolyte as the best porous structure. This is, however, only speculation, and this type of structure does not appear to physically feasible.

ST0264940

MORPHOLOGY

To study the morphology of the porous materials tested, a scanning electron microscope was used. The results were qualitative rather than quantitative and the results have to be qualified in the light of the limitations of the technique.

In general, the morphology is set largely by the fabrication technique, which, in most cases, produces a cohesive system formed by an open cell foam-like structure, i.e., vacuoles with breached walls. Fastening the cellular network together are hose and chain-like ribs which spread out in three dimensions. This is better illustrated in Figures 217 to 224. The different variations in the structure that can be found are -

1. Figure 217 - A dense continuous phase with open interconnecting vacuoles.
2. Figure 218 - Polymer particles, sintered together forming a chain-like matrix. This has the advantage of high porosity and surface area but since the particles are in general of magnitude smaller than the average pore size, there is a lower limit in the pore size attainable with this type of structure.
3. A variation of the structure shown in Figure 217 is shown in Figure 219. Here, the continuous phase is composed by flakes that appear fairly oriented in parallel plants.
4. Figure 220 shows an ionotropic isometric membrane that looks to be the closest to the idealized math model (1) already mentioned. Unfortunately, neither Kynar nor Teflon can be fabricated at the present in this form.
5. Dense membranes of very small pore size - The cracks or irregularities are only revealed by electron microscopy. The flow rates are high in general for this type of membrane due to the cracks, but the porosity is low.
6. Some membranes exhibit an aspect as shown in Figures 222, 223, and 224 and are fabricated by expanding gaseous vacuoles inside the material or by a solvent change. The vacuoles eventually burst forming an open path. Closed cells exist in type of membranes and may be a significant percent of the void space. This is undesirable for our purposes. Figure 222 shows a membrane with a significant amount of closed cells. In Figure223 , most of the cells are open, and Figure 224 shows a membrane almost entirely composed of open cells.

These examples were chosen as typical, well defined structures - in general, structures are not that well defined and will lie inbetween two or more of the types shown here.

FABRICATION

Ultrafiltration membranes are classified as dense or porous according to their void space content. Usually, not until the fraction of void volume becomes comparable to that occupied by the polymer, are they classified as porous. They differ only in the fabrication method. The main methods for obtaining porous membranes are -

1. Conversion of dense to porous membrane - These are produced by total immersion of the dense membrane in a swelling system followed by exchange of this system for a non-solvent medium. In most cases, the permeabilities are proportional to the concentration of the solvent in the swelling system. The limitations of this method are the sensitivity of swelling to solvent concentration, the loss of polymer substrate and the preparation of the original dense membrane. Purity of the solvent and controlled humidity atmosphere are also very important factors.
2. Fibrous Membranes - Producing paper or felt-like membranes, they are obtained from a suspension of fibers of the polymer. After draining and drying, the mat is callendered through press rolls to lower the water content and this is accomplished in most cases by heating. The fibers may remain relatively loose or may be annealed in order that bonds develop at the points of intersection. The main disadvantages are the difficulty to control pore sizes and of obtaining the suitable raw material in the form of fibers. Since the voids are, in general, larger than the diameter of the fibers, very low pore sizes require very small fibre diameters.

   An asbestos diaphragm is itself a membrane of this type in which a loose mat results. Polymeric films, in general, will not have structural integrity unless the fibers are fused or bonded together, fixing the structure.
3. Parchment Papers - Done essentially by the same process as before, the bonding step is done by means of a solvent that turns the surface of the fibers into a gelatinuous mass which sticks together on drying rather than by heating or compression. The solvent is washed away in some cases. In this process, part of the voids are lost, the results being greater adhesion and lower permeability.
4. Sintered Particles - This type of membrane is fabricated by bonding clusters of particles at elevated temperatures. The particles are heated to a temperature near the melting point of the substance and as the exterior surface of the particle softens or melts, capillary pressure tends to rearrange the solid particles. Densification and loss of surface area occurs together with decreasing surface rugosity of the particles. The process is more complicated than it appears to be and viscous or plastic flow, volume diffusion, surface migration and creep are involved.

S1028494

This process is largely restricted to polymers with a flexible configuration but it does not imply that actual surface melting is a requisite since sintering occurs in most cases without melting. The sintering temperature depends on the nature and the molecular weight of the polymer, crystallinity, the presence of additives, pressure and atmospheric humidity.

Sintering of loose granules result in weaker but more permeable membranes than the sintering of compressed powders. A non-sinterable additive may be present and is later extracted. In general, rapid heating produces a better produces a better product.

This process is suitable for materials for which an alternate process is not available, as for PFE, that is almost totally restricted to violations of this process. The membranes produced have a high strength and resistance to compaction, but their pore distribution is, in most cases, rather broad.

5. Extended Capillary Bundles - Producing cylindrical pores perpendicular to both membrane surfaces - this process is a recent development from hollow fibers technology. Although interesting, the technique does not appear to be applicable presently to the chlorine cell diaphragms.
6. Nuclear Track Membranes (Nuclepore) - This process includes radio-active bombardment followed by etching of the particle path. Very narrow pore size distribution are obtained, but the membranes are very thin, requiring some kind of backing in addition to being very expensive. It is doubtful that they can be available at the present time in large quantities.

The most convenient method to find pore volume and pore statistics was found to be the mercury intrusion method (5). The results appear to be reproducible within the limits of experimental error and the material reproducibility, but the analysis is troublesome and time-consuming. Figure 4 presents a mercury intrusion porosimeter curve for a Zitex membrane (E606-223) 6.5 mils thick, the curve tends to be shaped with a point of inflexion around the average pore size of 10 microns. An interesting result was found with Fluorotechniques (Teflon) membrane - the membrane M8R25000, rated 10 microns, yields the curve shown in Figure 5 while the membrane M7R1000, rated at one micron, gave the curve of Figure 6. It can be seen from both curves that the shape of the curve is about the same for pores over 20 microns and the net difference between both membranes is the percentage of small pores.

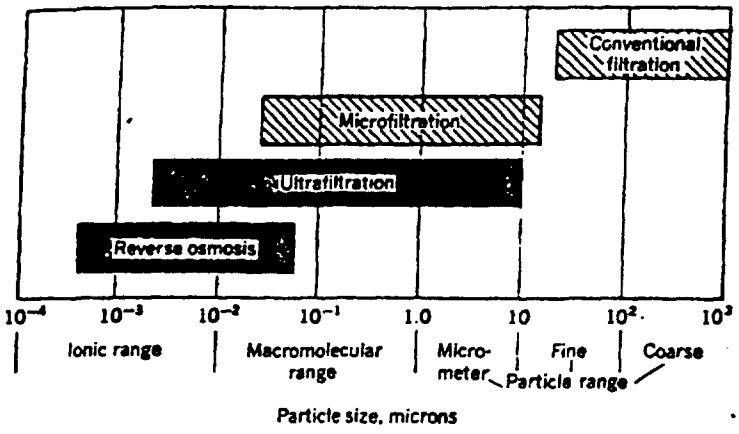
Although the M7R1000 membrane yielded the best overall results so far, the optimum membrane appears to be the one with the same type of distribution as for the M8R25000, but displaced to the right, with an average pore size of about 5 microns. These tests proved that the manufacturer cannot vary the pore size rating without changing, at the same time, the pore size distribution and that what is essentially varied is the pores under 20 microns.

S1026494

In addition, pore statistics may sometimes be misleading when the material is not homogeneous and presents a dense structure of low porosity at one or both surfaces or the small pores concentrate at the surfaces. In some cases, both effects are present and the surface of the membrane exhibits low porosity and low pore diameters. In a sense, it is desirable that the smaller pores be at the surface so that the membrane acts as a surface filter rather than a volume filter, but if this is accompanied by a dense film, undesirably high voltages occur.

ST0204943

Figure 1



Examples of particles retained by filter or membrane: Sodium, calcium, chloride, sulfate, other ions; sucrose, other small organic molecules; synthetic resins, antibiotics, hormones, enzymes, other large organic molecules; viruses; bacteria, yeast cells; colloidal clay, other finely divided suspensions; salt crystals, other precipitates; quartz grains.

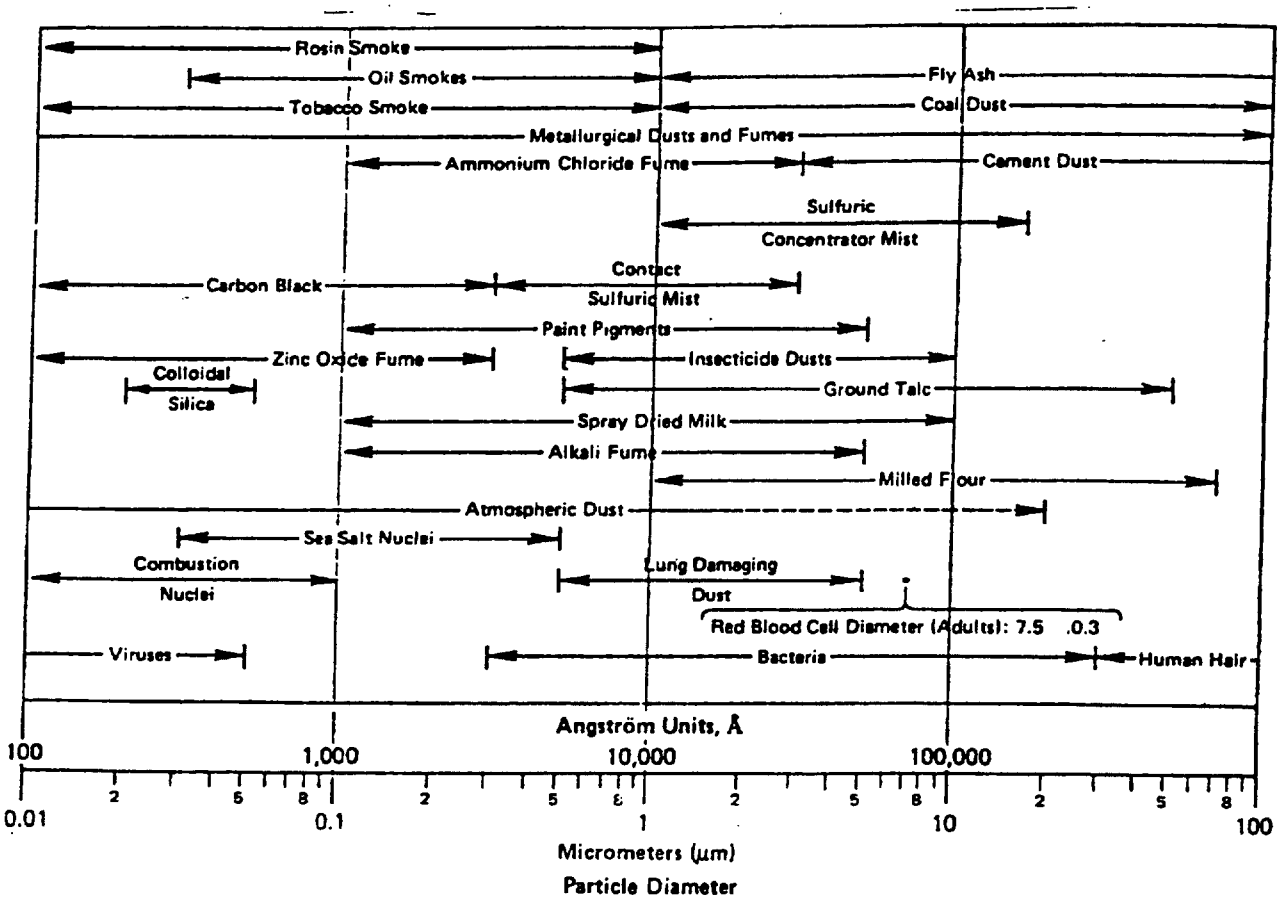
ST0284944

MEMBRANE SEPARATION PROCESSES

REPRODUCED FROM " SYNTHETIC POLYMERIC MEMBRANES"

R. E. Kesting, Mc Graw Hill New York 1971

Figure 2



3

PORE SIZES VS. COMMON PARTICLE SIZES

FOR DIFFERENT INDUSTRIAL PARTICLES, FUMES AND MISTS

ST0284045

Figure 3

Pl. III - 6

71 23949

2144102

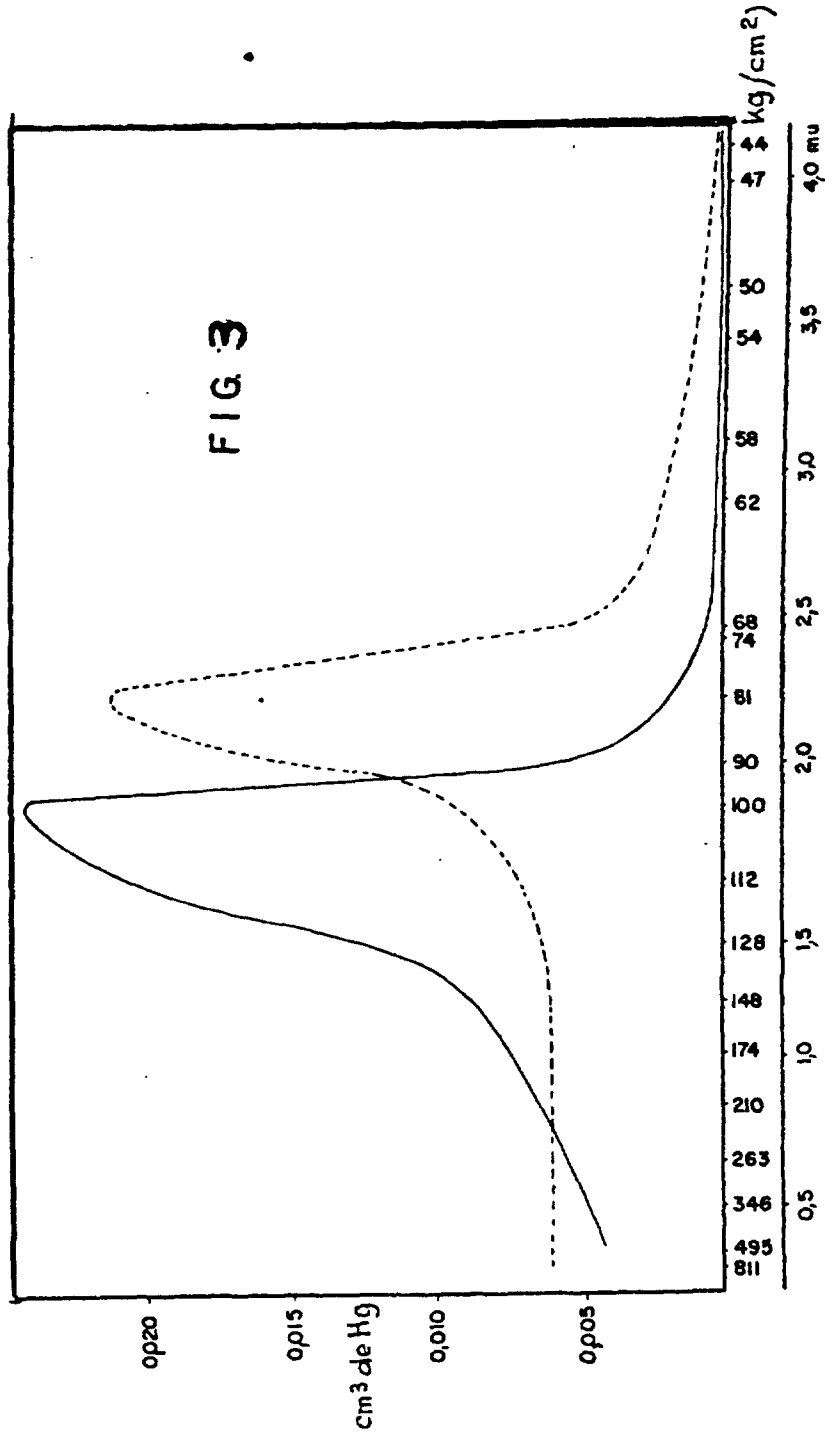


FIG 3

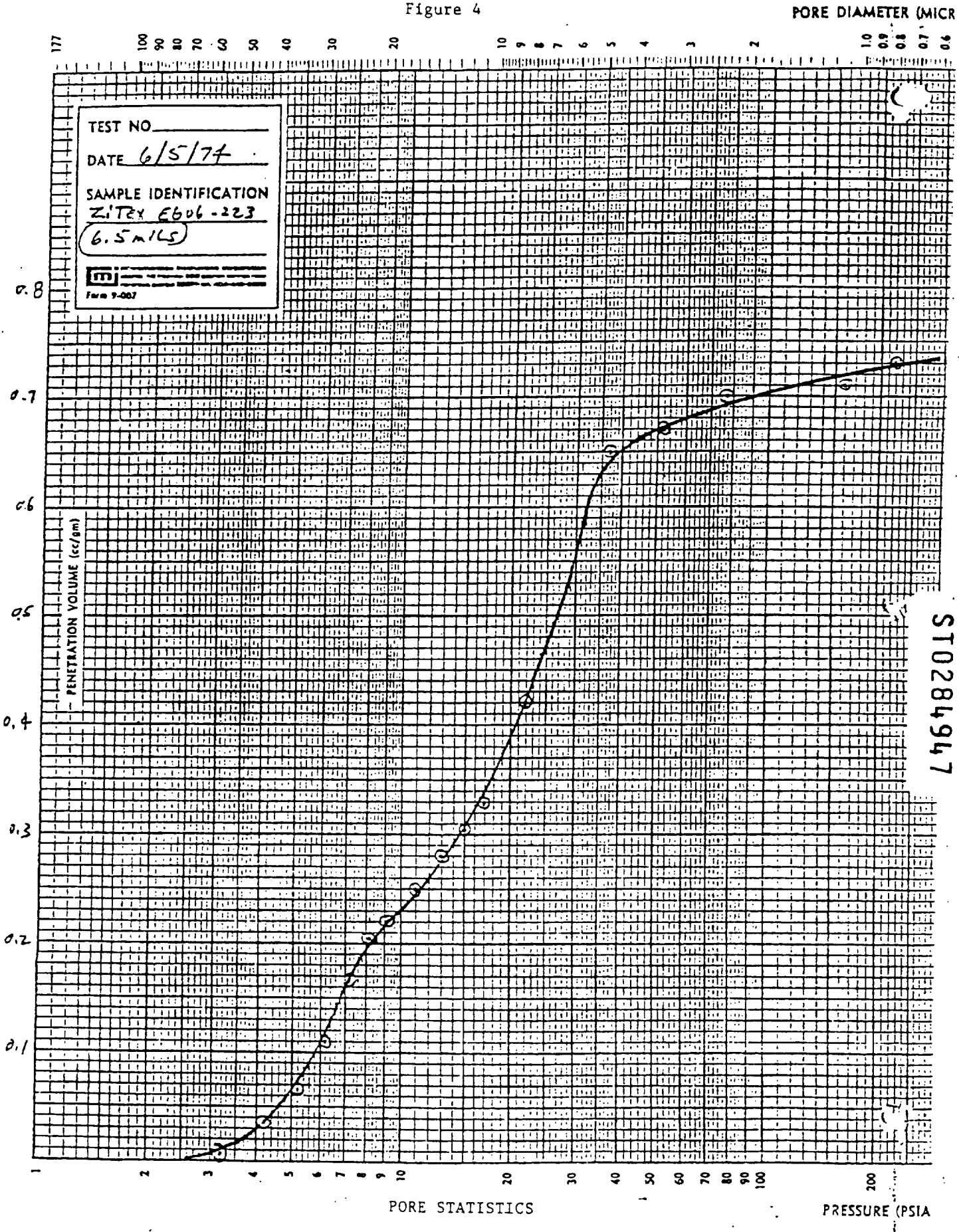
PORE STATISTICS

PORE SIZE DISTRIBUTION FOR A TYPICAL KYNAR MEMBRANE

REPRODUCED FROM BELGIUM PATENT 7123949

BE 802494

Figure 4



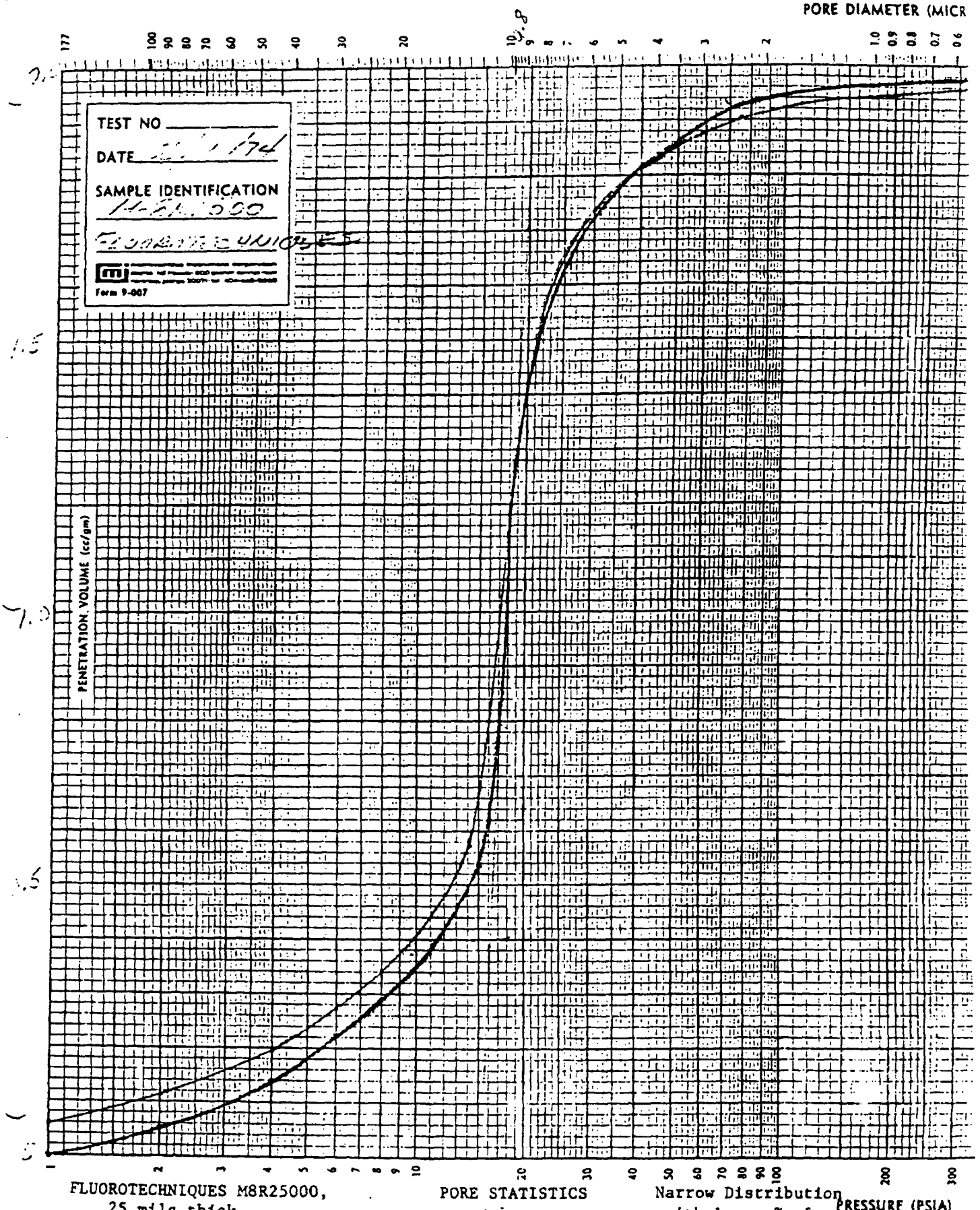
PORE STATISTICS

MERCURY INTRUSION METHOD

ZITEX E606.223 Porous Teflor
6.5 mils thick

ST0284948

Figure 5

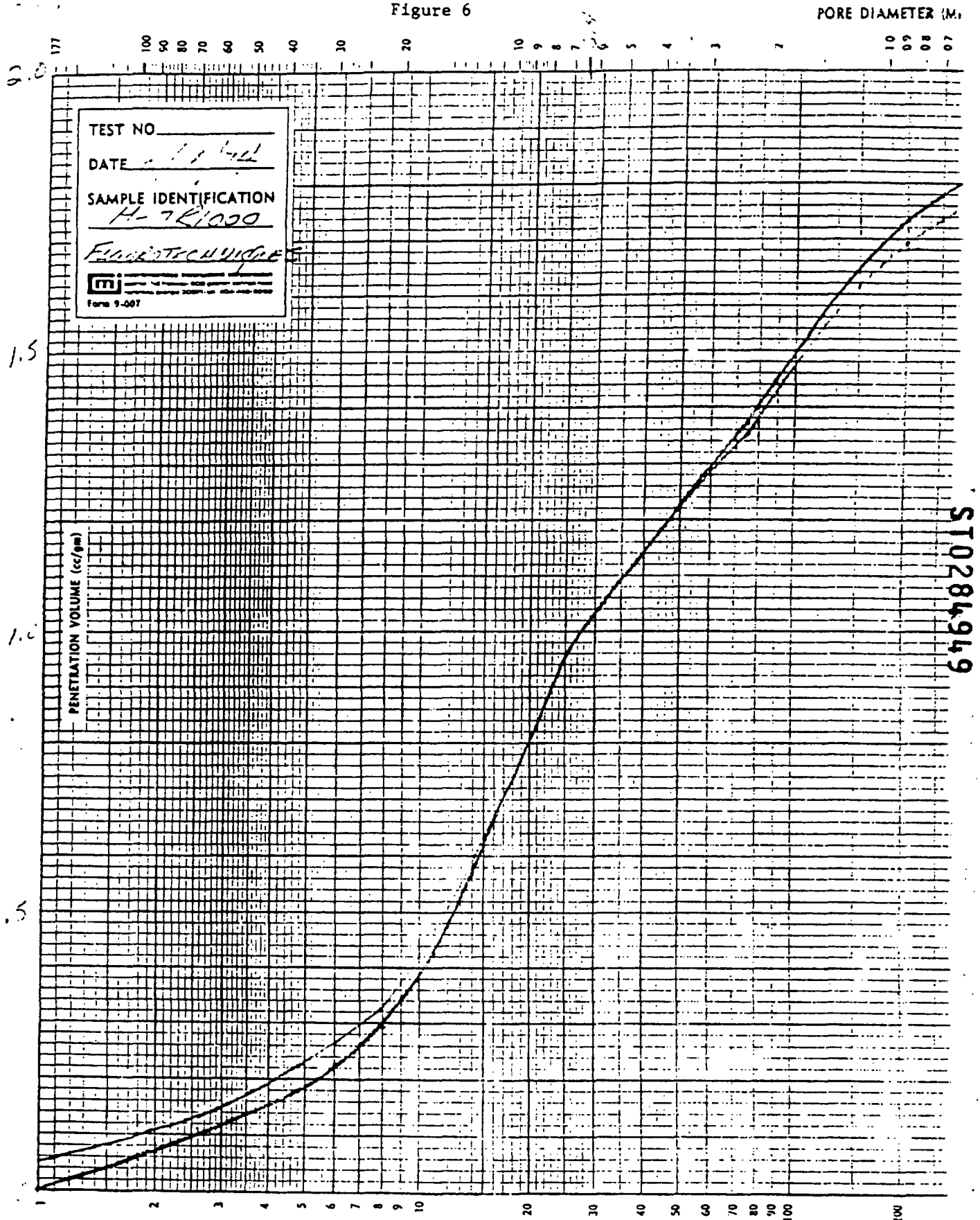


FLUOROTECHNIQUES M8R25000,
25 mils thick

PORE STATISTICS
MERCURY INTRUSION METHOD

Narrow Distribution
with large % of pores

Figure 6



FLUOROTECHNIQUES M7R1000
50 mils thick

PORE STATISTICS
MERCURY INTRUSION METHOD

ST0284949

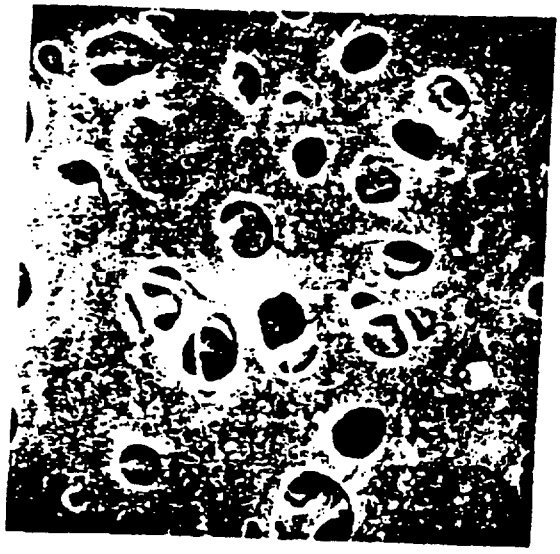


Fig. 2.17 Scanning electron photomicrograph of surface of cellulose acetate ultrafiltration membrane.

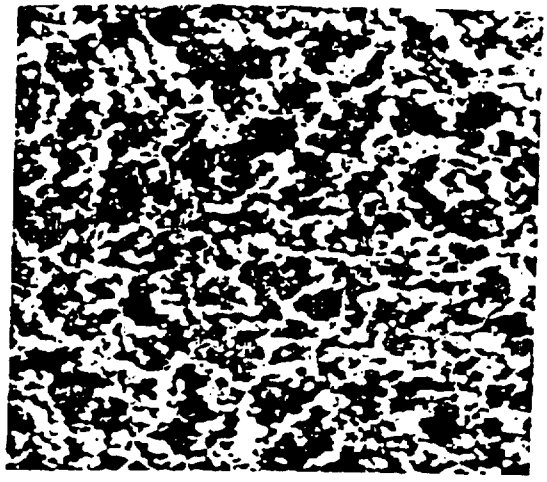


Fig. 2.18 Scanning electron photomicrograph of cross section of cellulose acetate ultrafiltration membrane.

ST0284950

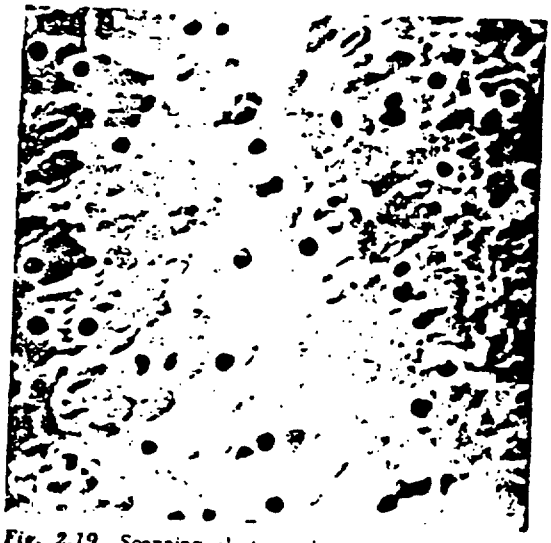


Fig. 2.19 Scanning electron photomicrograph of surface of nucleopore polycarbonate membrane.

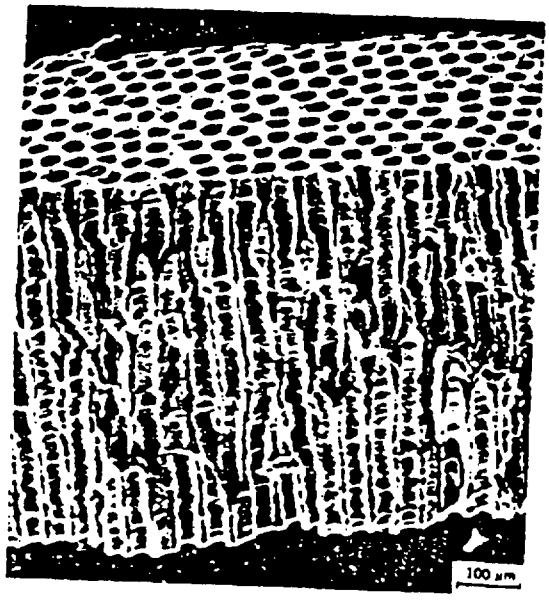


Fig. 2.20 Scanning electron photomicrograph of cross section of ionotropic gel membrane. (*Reimschuessel [51].*)

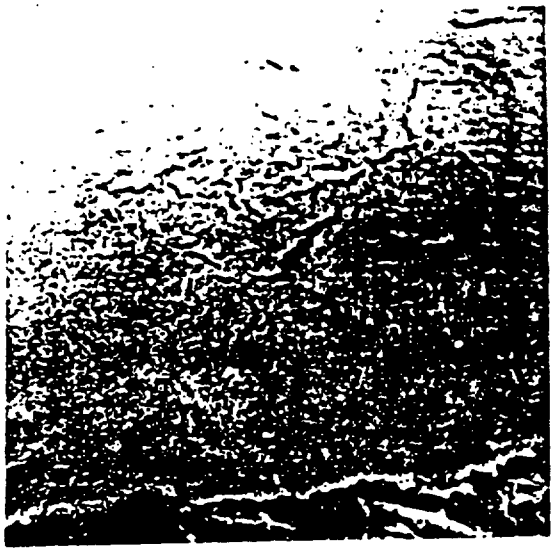


Fig. 2.21 Scanning electron photomicrograph of cross section of dense cellulose acetate membrane.

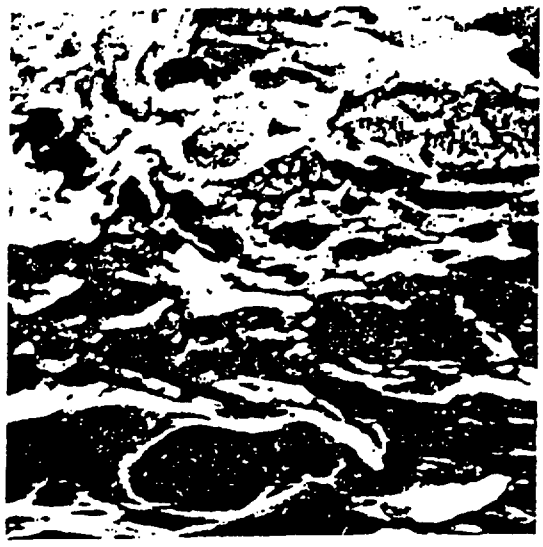


Fig. 2.22 Scanning electron photomicrograph of cross section of cellulose acetate membrane with closed cells.

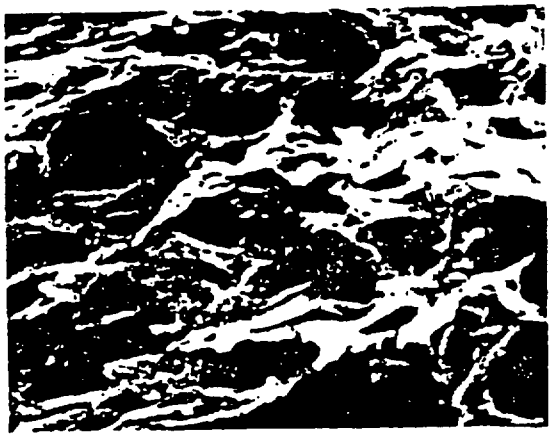


Fig. 2.23 Scanning electron photomicrograph of cross section of cellulose acetate membrane with open and closed cells.

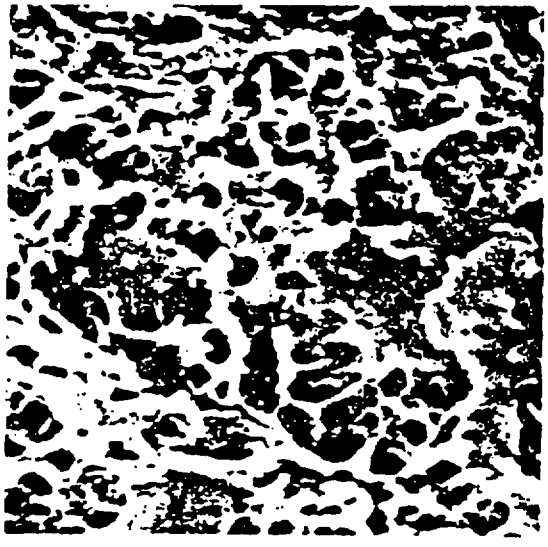


Fig. 2.24 Scanning electron photomicrograph of cross section of cellulose acetate membrane with open cells.

ST0284951

REFERENCES

(1) LAD-282 February, 1973.

(2) Synthetic Polymeric Membranes

(3) R. E. Kesting, Mc Graw Hill, New York, 1971.

(4) Belgium Patent 7123949

(5) Micrometric Instrument Corp.
Instruction Manual 900/910

ST0284952