Evaluation of the Effects Caused by a Variation of Parameters in a New Process for the Production of Microporous Polyethylene

by

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(ABSTRACT)

The effects caused by a variation of the key parameters involved in a proprietary process for the production of microporous polyethylene were investigated. The process involved the treating of a polyethylene film with two proprietary solutions at specific temperatures and in some cases required stretching of the material in the solutions.

Specialized equipment was developed to implement the process and determine the conditions under which porous material was produced. The effects of changing these process conditions on the porous nature of the material produced was then determined. It was determined that for the particular polyethylene film chosen for the investigation, the most uniform porous material resulted when the film was treated with the two proprietary solutions without the use of stretching. The conditions in the first solution were found to be the most important in determining the nature of the material produced. Pore size and distribution were not significantly altered in the variation of the parameters investigated.

The material produced had an average pore size of 0.17 micron and a pore density of 0.9×10^9 pores/cm^2. The yield point of this material was found to range from 610 - 840 psi (4.2 - 5.8 MPa).

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Chapter 1

Introduction

Industrial and medical applications of microporous and selective transfer membranes have been increasing as new materials and methods of production have emerged. Membranes of this nature have been used for years in kidney dialysis, blood oxygenation and vapor transmitting bandages in the medical field [1,2]. They have also found applications in industrial areas in pollution control, breathable chemical and water repellent fabrics, batteries, and fresh water from brackish or salt water separation [2,3,4]. Potential uses are numerous and increasing, and will provide increasing commercial interest in these types of membranes.

Currently the marketplace is dominated by membranes made of cellulose, polypropylene, polytetraflouroethylene and high-cost polymers. A commercially successful process has yet to be developed for the manufacture of these types of membranes from polyethylene. Because of the greatly reduced raw material costs, it is believed that a microporous polyethylene membrane could be of significant value in the marketplace. In this research, the important process parameters involved in a process for the production of a microporous membrane from polyethylene was investigated.

The proprietary process was developed by L. J. Arp in his home laboratory approximately four years ago and has been under investigation since that time. In the initial discovery, he noticed that an apparent structural change occurred in a polyethylene film when it was stressed while being exposed to certain chemical solutions. The resulting film showed a significant loss in translucence that seemed to indicate the development of micropores. The existence of these micropores was later verified by examination under an electron microscope. The solutions used in the process and the general conditions under which material of a porous nature would result were developed by Arp prior to the start of this work. The chemical composition of the solutions and film used are considered to be of substantial value in the market place and therefore are proprietary. This investigation was undertaken with the understanding that this information would remain proprietary.

The temperature conditions and dwell times in the solutions used for membrane manufacture were thought to be of importance in determining the porous nature of the resulting material. The stretching conditions used in manufacture were also thought to affect the porous nature. It was the goal of this research to determine the effects on the porous nature of material produced caused by changing these process parameters. Basic equipment for the manufacture and analysis of membranes was developed. Using this equipment and mostly empirical methods, initial, qualitative investigations into the specific process conditions that were needed to produce completely porous membranes were undertaken. Once these conditions were better understood, the quantitative effects of changing process parameters were investigated.

Chapter 2

Review of Related Processes

2.1 Introduction

A variety of processes currently exist for the preparation of microporous structures. The empirically developed techniques are usually shrouded in secrecy and have primarily been revealed in the patent literature. Kesting [5] has provided a fairly complete overview of most of the prevalent processes. This reference, along with the cited patents obtained from a search of the related areas, has provided the information contained in this review. In the discussion that follows, the key elements of each process is described. Applications of the method to polyethylene materials are then discussed.

2.2 Phase-Inversion Processes

Perhaps the most studied and well known technique for the preparation of microporous membranes is the phase-inversion process. Techniques of this type date back to the early 1920's with the development of finely porous cellulose membranes by Zsigmondy [6]. A multitude of variations on these techniques have been developed throughout the years and have become the most widely used for the production of microporous films and hollow fibers.

Phase-inversion refers to a process in which a three-component system consisting of polymer, solvents and pore-formers inverts into a two phase liquid-liquid system and then gels. The structure that results is one where the polymer has formed a microporous structure and the resulting pores are filled with the pore-forming material. Various pore-forming materials and techniques for solidification have been developed throughout the years. Kesting has grouped these into four areas: the wet process, the dry process, the thermal process and the polymer-assisted process. A discussion of each follows.

2.2.1 The Wet Process

Some of the earliest membranes produced were prepared by what has come to be called the wet process. One of the first patented processes using this type of technique was developed by Loeb and Sourirajan [7] for the preparation of wet, swollen, cellulose acetate membranes. In this process a solution of cellulose acetate, a suitable solvent, water, and a perchlorate salt was cast into a membrane and the solvent allowed to partially evaporate and form a two-phase gel. This was then immersed in cold water to form a wet gelatious membrane that after annealing, was suitable for desalination applications.

In the described process, the water and the perchlorate salt serve as the pore former. The immersion into cold water serves to solidify the membrane by exchanging a nonsolvent (water) for the polymer solvent by diffusion. Additionally, the immersion removes the salt used as a pore forming aid. The immersion into nonsolvent and the exchange of nonsolvent for solvent are the key elements in what is referred to as a wet process. Additionally, a wet process produces a wet gelatious membrane that in general, cannot be dried to yield a porous material.

A process of this type, for the production of microporous polyethylene, is not described in the literature nor is there any indication of the use of this technique with polyethylene.

2.2.2 The Dry Process

The dry or complete evaporation process, was developed by R. E. Kesting [8] for the preparation of dry cellulose acetate membranes. In this process, a solution of cellulose acetate, solvent and pore-forming material was first prepared. The pore-forming material used was a liquid nonsolvent with a boiling point 30°C higher than the boiling point of the solvent used. This solution was cast into a thin film. As evaporation of the solvent occured the solution inverted into a two phase liquid-liquid system and upon further evaporation, formed a microporous gel consisting of microporous polymer with the pores being filled with nonsolvent. The nonsolvent was then evaporated, leaving behind a dry microporous material.

The key element to this process and all dry processes is the complete evaporation of both solvent and pore former from the solution to form a dry microporous material. No techniques based on this method that are applied to polyethylene are described or referred to in the literature.

2.2.3 The Thermal Process

One of the more recent advances in the technology is the thermal inversion technique developed by Castro [9]. He discovered that a microporous structure could be produced from a great variety of materials using this method. The process began with the formation of a homogeneous solution of polymer and a latent solvent, (a latent solvent is a liquid that is a nonsolvent at low temperatures and a solvent at high temperatures). The solution created was formed into the desired shape and cooled at a rate such that the thermodynamic conditions initiated a liquid-liquid phase separation. The cooling was continued and gelation and solidification of the structure resulted. The latent solvent was then removed.

The structure resulting from the process was a homogeneous cellular form consisting of tiny spherical microcells with adjacent cells interconnected by small passageways. Perhaps the best feature was the uniformity of the material.

Castro successfully applied his process to both high and low density polyethylene using a multitude of compatible liquids. The resulting material was highly porous with void volumes of 30 to 80 percent. The pore sizes were said to typically range from 0.1 to 5 microns with 0.2 to 1.0 micron being more typical. The structures may be made in the form of not only thin films, but also in the form of blocks and intricate shapes.

2.2.4 The Polymer-Assisted Process

A variation on the phase-inversion process that uses a leachable polymer as the pore former was developed by Kesting [10]. The process was developed for the preparation of polyester membranes and was referred to as a polymer-assisted phase-inversion process. The process began with the creation of a homogeneous solution of two physically compatible polymers and solvents. The solution was cast into a film. As evaporation of the solvents occurred the liquid-liquid phase separation was initiated. Partial or complete evaporation of the solvents was then allowed to occur depending on whether a wet or dry process was to be employed. The film was immersed in a liquid which is a solvent for one of the polymers but not the other and the leachable polymer was removed. The resulting structure was a fine microporous structure with the pore size determined by the nature and the quantity of the assisting polymer. The literature shows no process of this type for the preparation of microporous polyethylene.

2.3 Leaching-Type Processes

A closely related process to the polymer assisted phase-inversion process is the leaching process. Techniques of this nature are also old, and date back to the late 1960's. In these types of processes a leachable substance is blended together with the base polymer and formed into the desired shape using common forming techniques. A selective solvent is then used to remove the leachable substance and leave behind a porous network structure. Various leachable substances are employed in this type of process. They include surfactants [11], plasticizers and hydrocarbons [12,13], chloroflurocarbons [14] and other polymers [15,16].

These types of processes have been applied very successfully to polyolefins and polyethylene in particular. The patent literature is filled with descriptions of various types of these processes using the fillers previously mentioned. Besides the use of different leachable substances, these types of processes include unique processing steps to produce structures of varying nature.

Micheal Rock [12] has employed the use of an intermediate solvent to reduce the shrinkage of pores that occurs when the extraction solvent is evaporated from the porous polyolefin film. In this process, after the leachable fillers have been removed from the formed material, the film is immersed in a solution in which the extraction solvent will readily mix. The removal of the solvent from the structure is therefore accomplished by diffusion into the intermediate solvent rather than by evaporation. It is often useful to make this intermediate solvent the final liquid in which the membrane will be used.

Shinomura [16] has employed post stretching of polyolefin membranes at elevated temperatures to generate desired pore structures. In his process, it is this stretching after the extraction that actually generates the micropores. After blending two compatible polymers into a sheet of desired thickness, a selective solvent is used to remove the leachable polymer. The material that results is not microporous, but after stretching at elevated temperatures, develops a system of micropores. It is believed that the extraction provides sites for the formation of pores that are generated by the stretching.

In general, the extraction time of these processes can be substantial and the forming of heavily filled incompatible substances can be difficult. No significant commercial success of leaching-type processes has been achieved.

2.4 Swollen Dense Films

A unique method for using a swelling solution for the preparation of membranes of varying permeabilities was developed by Brown [17] for use with collodion membranes. Dense membranes were immersed in a swelling solution and then transferred in their swollen state to a nonsolvent system. In his experiments, varying concentrations of water-alcohol solutions were used to vary the degree of swelling of the collodion membranes. These membranes were then washed in water to remove the swelling medium. He found that the permeability varied regularly with the strength of the alcohol in the swelling solution. He believed that he could extend his experiment to make extremely porous membranes, but concluded that they would be structurally very weak.

A similar technique was developed by Michaels et al. [18] for varying the permeability of polyethylene. In this technique, polyethylene film was swelled in p-xylene and annealed at elevated temperatures in the swollen state. Through the application of this technique, the rate of xylene liquid permeation through the membrane was increased. It was believed that the technique opened new prospects for the tailoring of polymeric materials for separation purposes.

2.5 Overview of Processes

From the review of the current methods being used for the manufacture of microporous materials, there appears to be a current need for a process that can be economically applied to polyethylene. The phase-inversion techniques have been successful with polyethylene only using the thermal process; the structure produced is of a form that may not be desired in many applications. Swollen dense films of polyethylene have not been produced that contain micropores. The leaching type processes have been applied to polyethylene but often require extensive extraction times or the use of fillers that make processing difficult. The technique under investigation in this research provides a means of producing microporous polyethylene which does not require extended solution treatment times. The material used in the process is a commercially available melt-extruded polyethylene film. The pore structure that is produced is unique, unlike that produced by the thermal inversion technique. This process may therefore fill the need for for an economically viable process to produce microporous polyethylene. An investigation into the effects of changing the important process parameters on the nature of the material produced from this process is appropriate.

Chapter 3

Equipment and Methods

In order to investigate the effect of varying important process parameters, several pieces of specialized equipment were needed to (1) control solution bath temperatures, (2) provide for controlled stretching, and (3) evaluate the materials produced . Additionally, membrane analysis techniques needed to be developed. A review of this equipment follows.

3.1 The Temperature Control Bath

From preliminary investigations, it was determined that a fairly precise system for the control of proprietary solution temperatures would be required. The system needed to be capable of handling a sufficient quantity of solution to fully immerse the stretching device, to provide uniform heating, and keep to temperatures within about 1°C of the desired temperature. A small, temperature-controlled water bath with a simple on-off type controller was sufficient to meet these needs. A drawing of the system developed is shown in Fig. 1.

Dimensions were based on what would be required to contain the stretching device. Approximately 3 gallons of ordinary tap water were contained in the outer bath to supply heat to the solution bath. Solution temperature needs were on the order of 60° - 80°C and system losses were expected to be substantial because of evaporative losses. A considerable heat input was deemed necessary to allow adequate control of the large quantity of fluid. A total of 2,000 watts was input via two standard 120-Volt hot water heater elements. These elements were controlled by a Fenwal model 17100 thermoswitch and a 120-Volt relay. The bath temperature was kept uniform by continual stirring at a point midway between the heating elements. The resulting system was found to keep temperatures to within about 0.5°C of the set point temperature. This was thought to be sufficient for experimental needs.

3.2 Stretching and Restraining Devices

A means of controlling the manner in which material was stretched in the heated solution was also needed. The device had to provide uniform uniaxial stretching of the material and allow for adjustments to the rate of stretch and the amount of elongation. The samples produced needed to be of sufficient size to allow for analysis of the material. A circular disc of material with a 1.5-in. (3.8-cm) diameter was required for this purpose. The operation of the device could not introduce temperature fluctuations in the solution bath. The device designed to meet these needs is shown in Fig. 2.

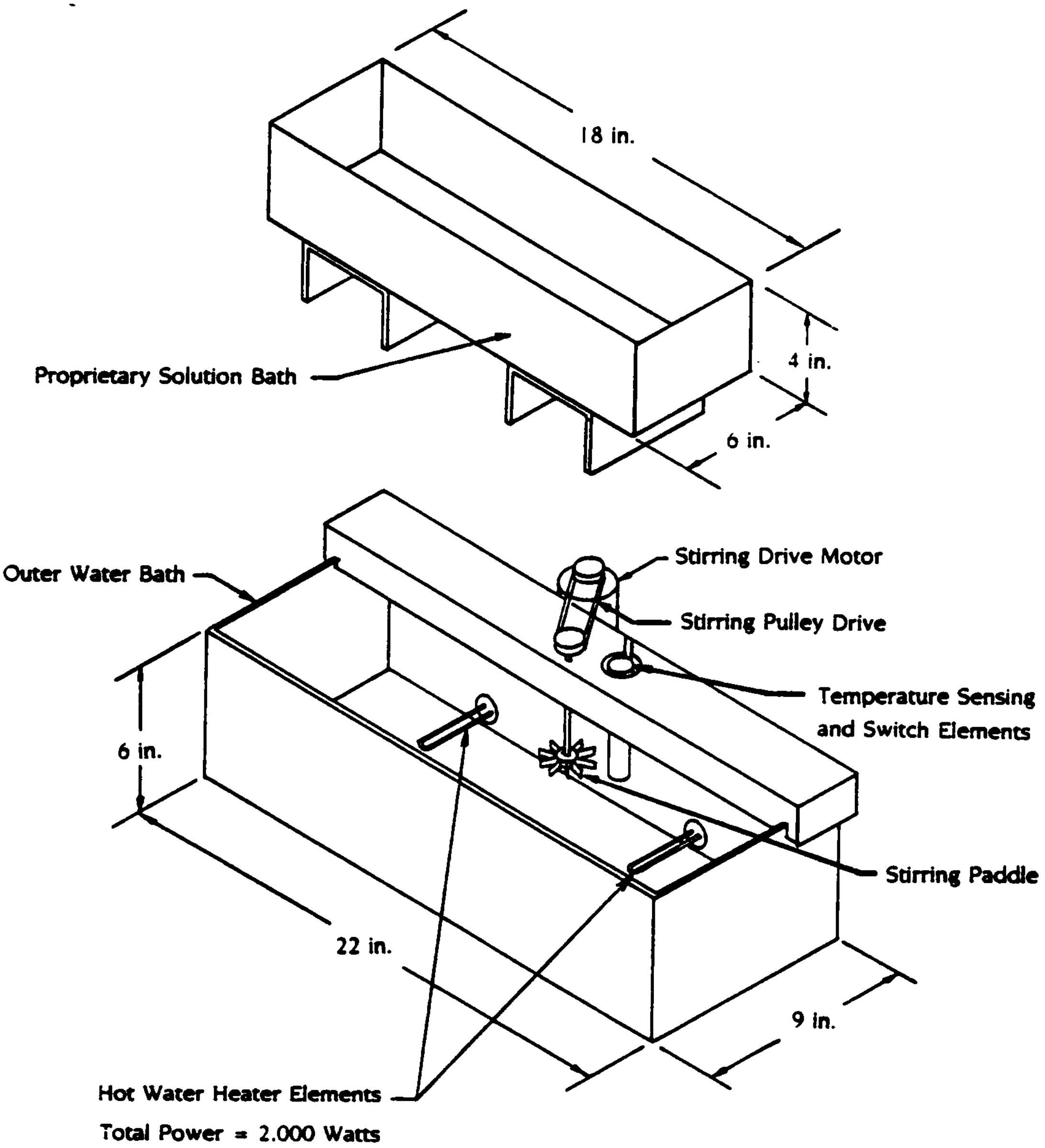

Figure 1. Temperature-Controlled Bath

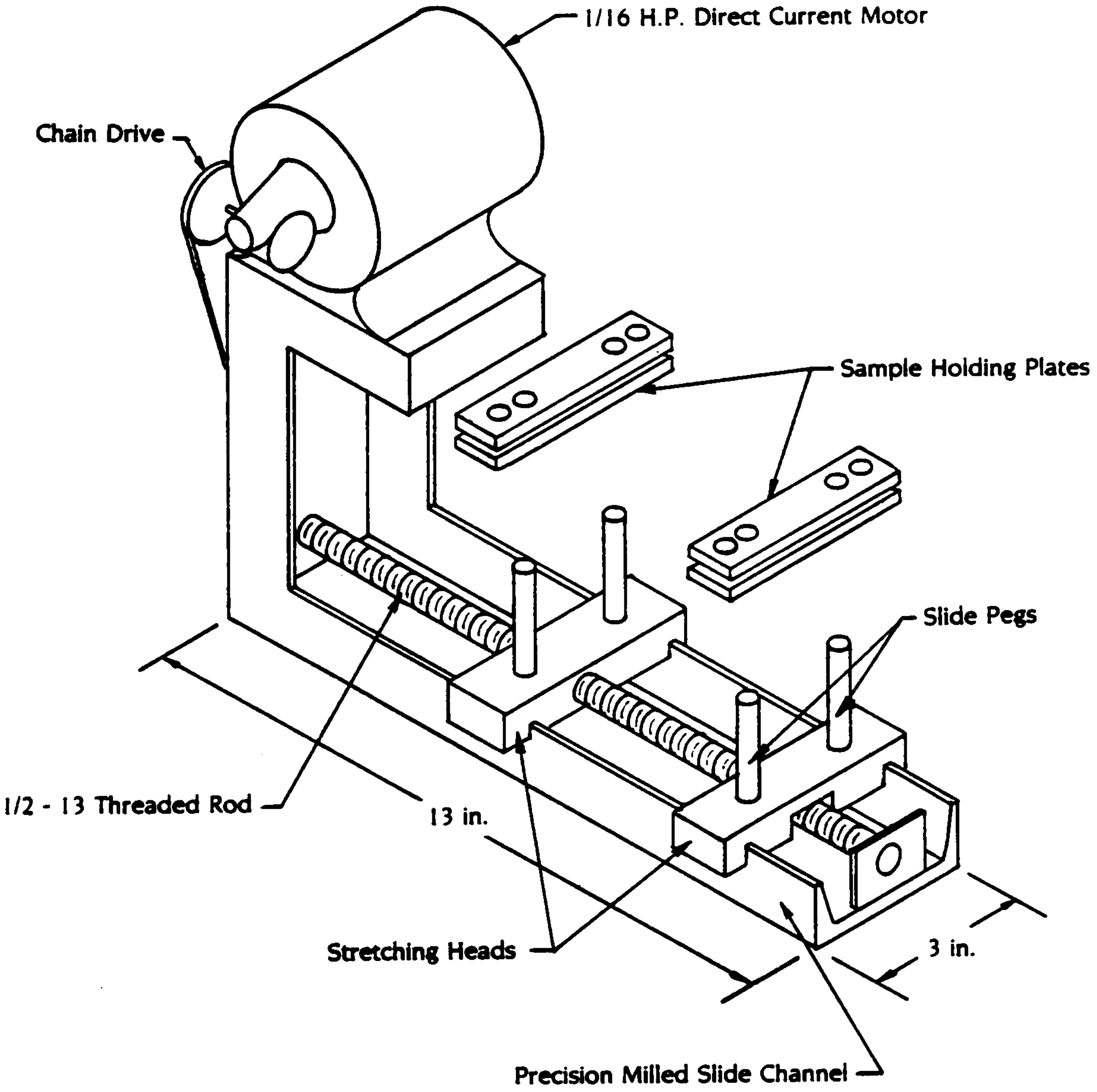

Figure 2. Stretching Device

A sliding stretching head on a precision milled channel was used to provide uniform parallel uniaxial stretching. It was driven by a threaded rod which was chain-driven from a variable speed direct-current motor. The motor was mounted a sufficient distance from the solution to allow for easy removal of the samples. Adjustment of motor speed by changing the power supply voltage was used to adjust stretch rate. A limit switch was used to stop the motion of the stretching head at the same location for each test. Adjustments to the initial sample size were used to adjust the percent stretch. Sliding pegs were mounted to the stretching heads and two matching sample holding plates rode on these to provide a means of sample immersion and removal. The final device provided the desired control required to investigate stretching parameters, though experimentation would later show that stretching did not significantly alter the pore size or distribution.

To restrain the membranes in their stretched condition while they were setting, the clamping frame shown in Fig. 3 was developed. The clamp was designed to fit between the stretching heads when they were at a 2-in. (5-cm) spacing. This was the spacing used to obtain the maximum stretch used in the investigation. The clamp was held cradled in the slide channel with four pins that extended from the bottom side of the clamp. During stretching, the clamp was held open by two spacing bars that were removed after the elongation was completed. The wing nuts were then quickly tightened and the membrane restrained while drying.

3.3 Membrane Preparation Procedures

A sample of the plastic material to be used was prepared and clamped within the sample holding plates. The sample size was determined based on the stretch

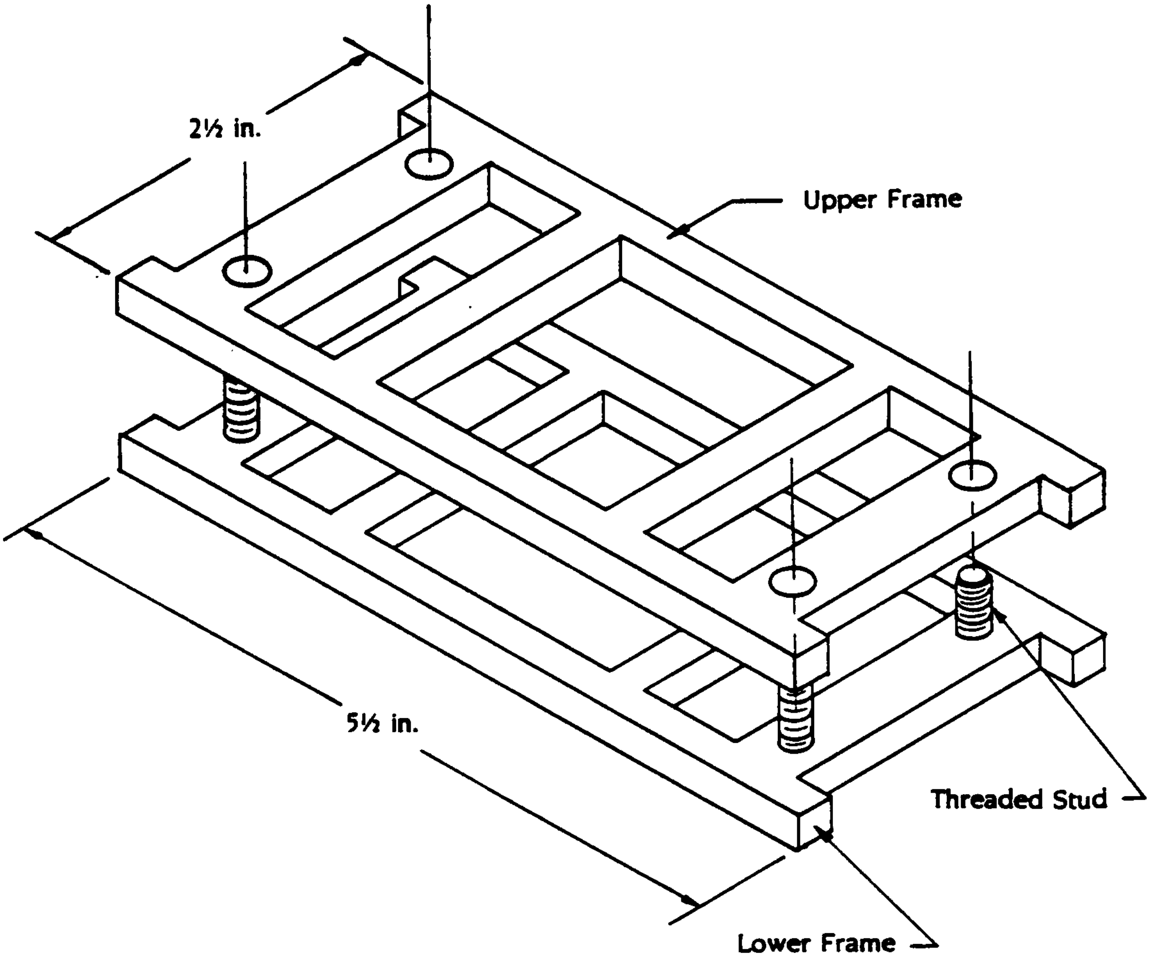

Figure 3. Clamping Frame

conditions that were to be used in the process. The sample was always 3 in. (7.6 cm) wide. The length of the sample between the plates was set to obtain the desired percent stretch with a resulting 8 in. (20.3 cm) final length.

Figure 4 is a drawing of the processing equipment used for membrane preparation. Before immersion into the proprietary solutions, bath temperatures were measured and recorded to within 0.5°C using mercury thermometers. The sample was then immersed into proprietary solution 1 and stretched when required. The soak time and stretch time were measured to the nearest second and recorded. If a drop in the solution temperature of more than 1°C had occurred during the procedure, the trial was not used for quantitative results.

The material was then removed from proprietary solution 1 and immersed in proprietary solution 2. The transfer time was measured to the nearest second and recorded. The material was then allowed to soak in solution 2 for the desired period of time. Upon removal from the bath, the sample was allowed to air dry and the bath was checked for significant temperature changes. For each set of processing conditions that were investigated, a minimum of four trials were made.

3.4 Material Testing Equipment and Procedures

The evaluation of the materials that were produced from the process needed to include methods to: (1) determine if the material was porous, (2) determine the pore size and density of the structure that was present and (3) determine whether results were repeatable.

The apparent color of a membrane which has been produced from a clear plastic can be used as the first indication that micropores have been developed. With

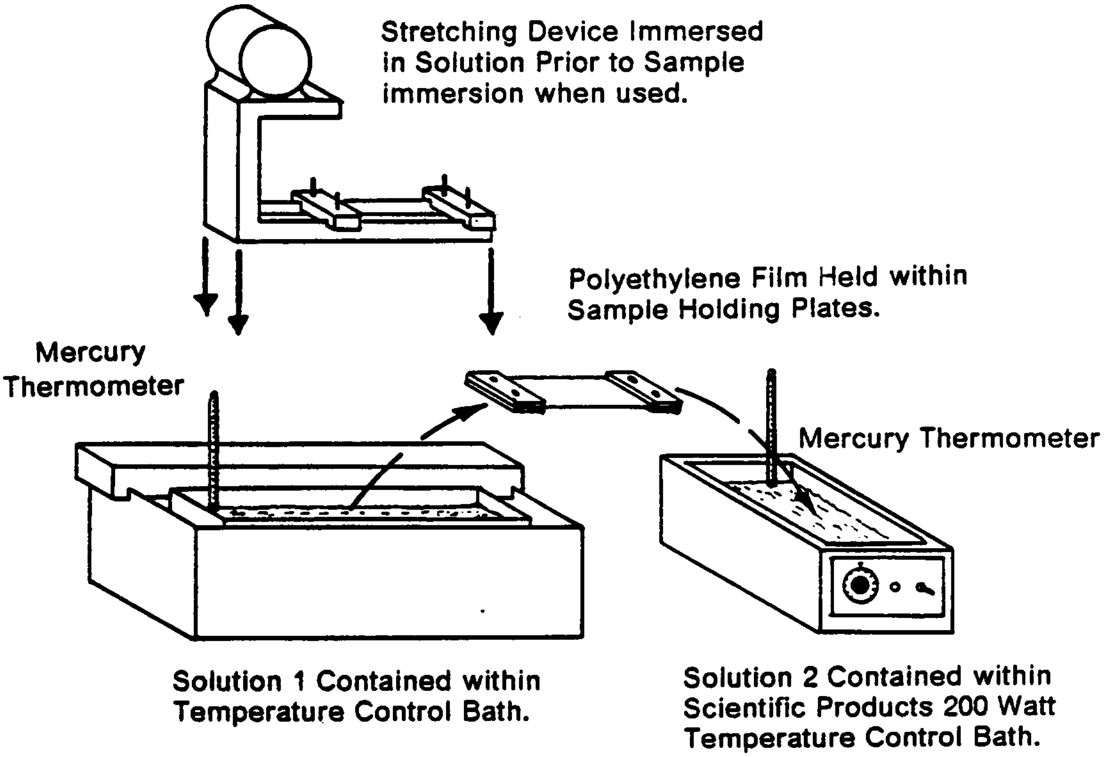

Figure 4. Membrane Processing Equipment

polyethylene, the development of micropores is accompanied by a change in color from a clear waxy appearance to a flat milky-white appearance. Initial evaluation of the materials which were produced was therefore done through a visual examination of the degree and uniformity of the clouding in the membrane.

Direct observation of the membranes produced under the scanning electron microscope could have been used to both verify porosity and determine the pore size and density in the material. Because of the great expense involved in the use of this equipment, a simple preliminary evaluation method was needed. Using the principles of Hagen-Poiseuille flow and the bubble point method, a simple test was devised to detect changes in the pore structure from changes in the rate of fluid permeation through the membrane. Using the results of this simple test, samples were then chosen for examination under the scanning electron microscope. Both surface and cross sectional samples were prepared and viewed to determine the nature of the material produced.

3.4.1 The Hagen-Poiseuille Model

In order to understand the principles on which the test was based, a review of the nature of flow through porous medium is in order. One simple method which can be used to describe the flow, models the porous structure as a series of uniform pathways through the solid structure as shown in Fig. 5. In most membranes, these pathways are not straight and tubular, but are tortuous and varied in length. It would be difficult to obtain an accurate description of the average path that is taken by any fluid particle passing through the membrane. As an approximation, the thickness of the membrane is used as the capillary length and pathways are considered to be straight. This allows the flow to be modeled using relationships developed for flow

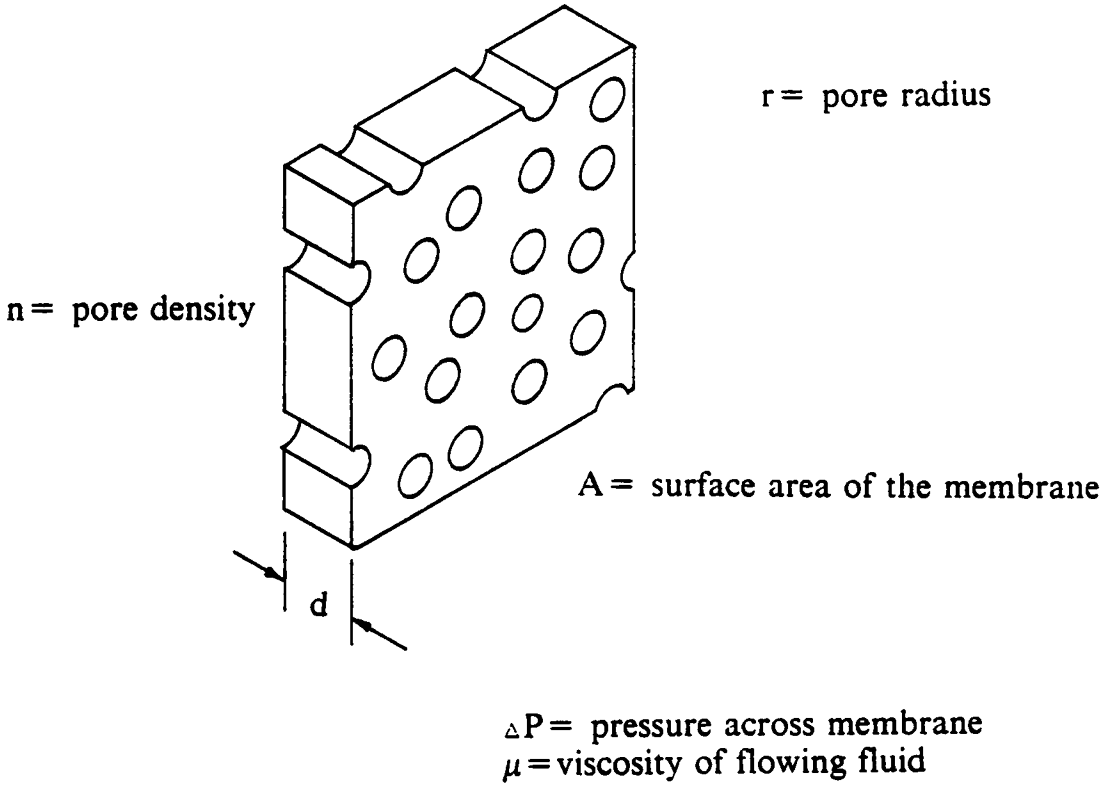

Figure 5. Simple model of a porous membrane.

in tubes. In the majority of cases, the fluid flow rate through the material is very low and laminar flow is present. (After development of the equations based on this assumption, this will be shown to be very reasonable.) If the flow is laminar, it can be modeled using Hagen-Poiseuille flow relationships in a series of parallel capillary tubes. Using this approach, the flow through the membrane can be described as follows:

$$J = \text{effluent flow rate} = \frac{n\pi r^4 A\Delta P}{8\mu d}$$

Where,

$n =$ pore density (pores/cm^2)

$A =$ surface area of the membrane (cm^2)

$\Delta P =$ pressure across membrane (Pa)

$\mu =$ viscosity of flowing fluid (kg/m-s)

$d =$ thickness of the membrane (cm)

$r =$ pore radius (cm).

Based on this model, if all other factors remain unchanged, a change in the pore size or pore density results in a significant change in the rate of fluid permeation through the material. The measurement of the rate of gas flow through the membrane should give an indication of the nature of the pore structure and specifically indicate changes that have resulted and should be viewed under the scanning electron microscope.

It should be recalled, that this model has been based on the assumption of laminar flow through the membrane. Verification of this fact can be obtained by determining the typical order of the Reynolds number assuming some typical pore structures. Typical microporous membranes have pore radii on the order of about 0.1 micron and pore densities on the order of about 1×10^9 pores/cm^2. If we assume a pressure across a 0.01-cm thick membrane of about 70 kPa, the flow through the membrane would be:

$$J = \frac{(1x10^9)(\pi)(0.00001)^4(1)(70,000)}{8(1.8 \times 10^{-5})(0.01)}$$

$$J = 1.5\,(ml/\sec/cm^2)$$

The flow through any one pore would be on the order of 1.5×10^{-9}. ml/min. The mean velocity in any pore would be on the order of 0.05 m/sec. The Reynolds number based on tube diameter is given by:

$$Re = \frac{\rho VD}{\mu}$$

where

ρ = density of flowing fluid (kg/m^3)

V = mean velocity (m/sec)

D = tube diameter (m)

μ = viscosity of flowing fluid (kg/m-s)

Using the typical values, the Reynolds number is found to be on the order of 0.001. This is many orders of magnitude less than the critical value of 2300 which marks the transition from laminar to turbulent flow.

3.4.2 The Gas Flow Testing Fixture

To measure the flow through the prepared membrane, a gas flow testing device was developed. The device required the use of a sufficiently large sample of material that would be representative of the specific membrane. The sample needed to be of sufficient size to provide a measurable flow rate at pressures that would not alter the membrane structure. A 1.5-in. (3.8-cm) diameter sample using the center 1.0-in. (2.5-cm) diameter as the test area was sufficient to meet these needs.

The test fixture developed for this purpose is shown in Fig. 6. Compressed air supplied to the pressure chamber permeates through the membrane sample which is sealed between the lip in the base structure and the brass sieve plate. The gas that permeates through is collected in the O-ring sealed collection chamber in the upper cap. The brass sieve plate is included to provide structural support so that the membrane is not deformed under the testing pressure. A drawing of this plate is shown in Fig. 7. The total open area is 0.41 in^2 (2.7 cm^2).

The entire setup used to conduct the gas flow tests is shown in Fig. 8. Compressed air was supplied to the test fixture through the regulator and the delivery pressure measured using a mercury manometer. The collection tube ran from the fixture to a position 2-in. (5.1-cm) deep in a water filled collection pan. The collected gas was bubbled into a water-filled graduated cylinder for volumetric measurements.

3.4.3 The Standard Flow Test Procedure

From each preparation trial, two samples were removed from the material. Each membrane was seated into the test fixture and the upper cap sealed finger tight with wing nuts. The air supply valve was then opened and the pressure regulator used to adjust delivery pressure to 6 in Hg (152 mm Hg) as was indicated on the mercury manometer. After the flow had stabilized and a uniform stream of bubbles appeared from the collection tube, a water-filled graduated cylinder was positioned over the collection hose. The size of the cylinder was chosen to be 10, 25, 50 or 100

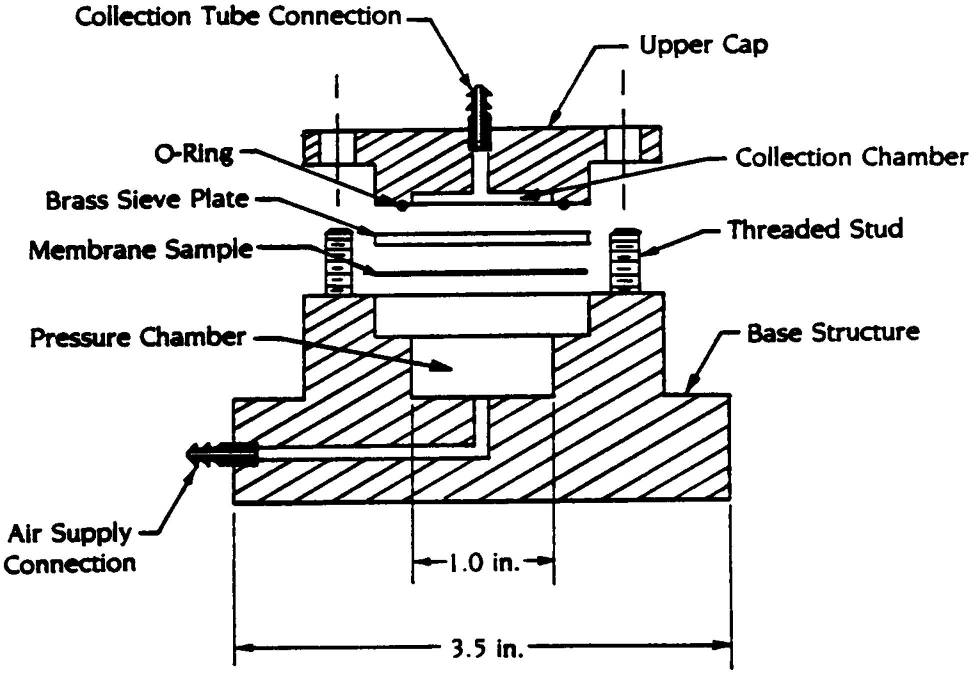

Figure 6. Gas Flow Test Fixture

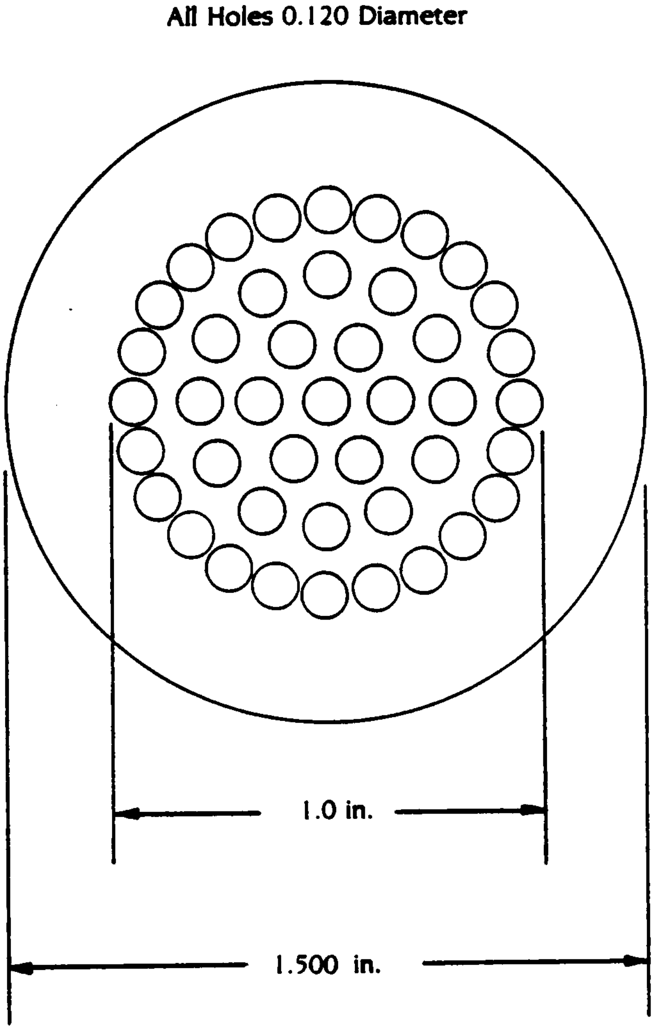

Figure 7. Brass Sieve Plate

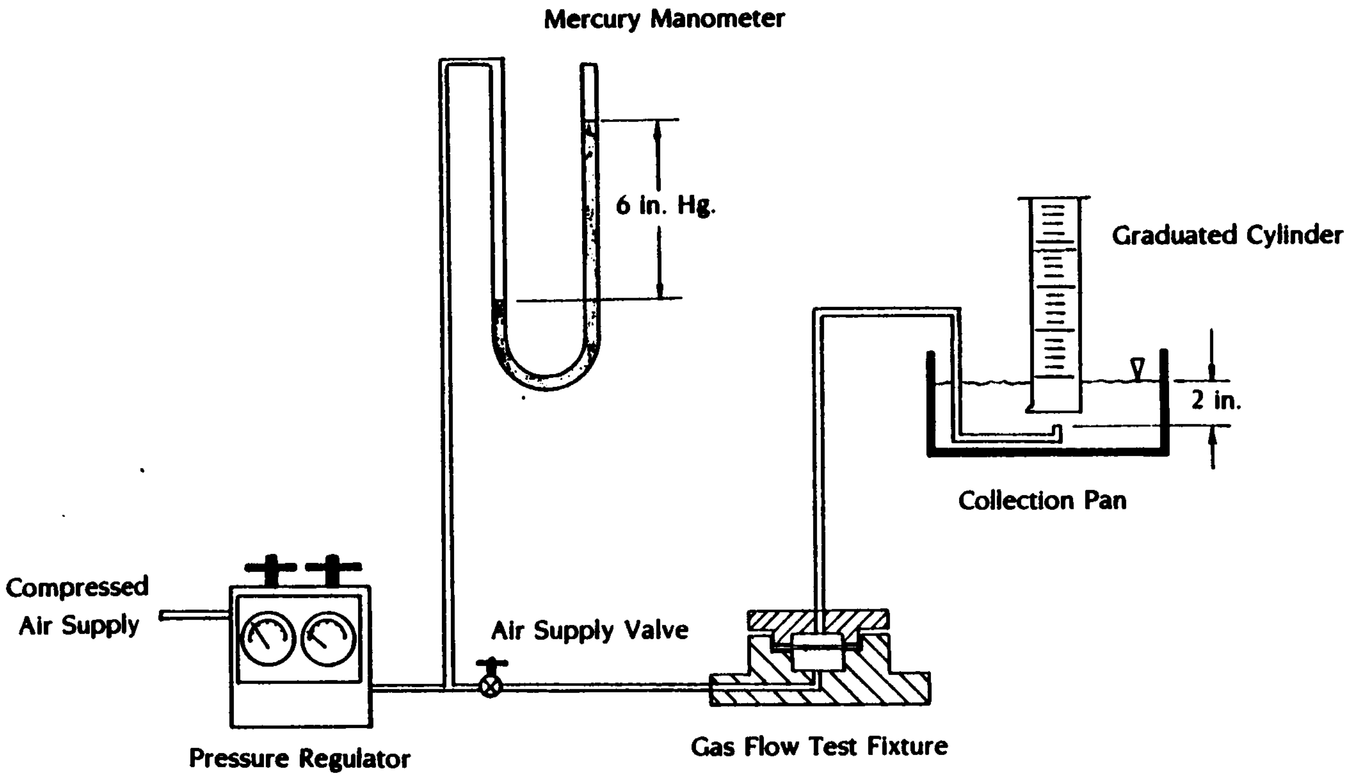

Figure 8. Standard Flow Test Equipment

ml depending on the estimated rate of bubbling from the hose. The time to completely displace the liquid from the graduated cylinder was measured to the nearest second using a stop watch. The gas flow rate was then calculated and the two samples averaged to yield the mean membrane flow rate.

A secondary open cap -- prepared to seal the membrane in place but allow viewing of the membrane surface -- was used to check for suspected pin holes. The technique used was based on the bubble point method. The surface of the membrane was wetted with isopropanol which was drawn into the membrane structure. A pressure of 10 in Hg (254 mm Hg) was applied to the membrane. If a pin hole was present, this pressure would be sufficient to clear the pin hole passageway and allow air to bubble through the membrane. If no pin holes were present, the surface tension of the isopropanol would be too large to allow the clearing of the tiny passages and no air would to pass through the membrane.

3.4.4 Sample Preparation for Electron Microscope Viewing

It was not economically possible to view and photograph samples from every trial run. The samples chosen to be viewed were only from trials where significant differences in flow characteristics were measured. From the set of membranes produced under a given set of conditions, those samples with measured flow rates close to the average and with a uniform coloration were chosen to be viewed.

A sample approximately 5-mm square was cut from the center portion of the tested membrane disc and mounted on an aluminium stub with double-sided tape. For cross sectional views, the membrane disc was frozen in liquid nitrogen before the sample was removed. A fractured edge was produced by cutting and tearing the sample. This was then mounted on a 45° angle aluminium stub. Prepared samples were then sputter coated with approximately 120 angstroms of gold.

Samples were inserted into the scanning electron microscope and scanned at a magnification of 1,000-2,000 to examine the structural uniformity. After locating a representative area, a photograph at a magnification of 10,000 was taken for pore sizing and counting purposes. If significant differences were not seen between a viewed sample and previously photographed samples, no photographs were taken. For cross-sectional samples, side views at a magnification of 1,000 were also photographed to show the complete cross section as well as at a magnification of 10,000 to show the pore structure.

3.4.5 Pore Counting and Sizing Techniques

A 10,000-magnification photograph of the surface of the membrane to be analyzed was used for pore counting and sizing purposes. A typical photograph is shown in Fig. 9 with the actual pores outlined in white. A template was prepared which contained a 2-cm by 2-cm square open area through which the photograph could be viewed. This template was positioned over the photograph as shown in Fig. 9. The pores within the square region were sized and counted. Sizing was done with the use of dividers and a scale to the nearest 0.1 micron. This corresponded to the nearest 1.0 mm on the photograph. This procedure was used to size and count the pores in ten different regions of the photograph. Using the pore sizes and the pore counts from the ten regions, the average pore size and average pore density were determined.

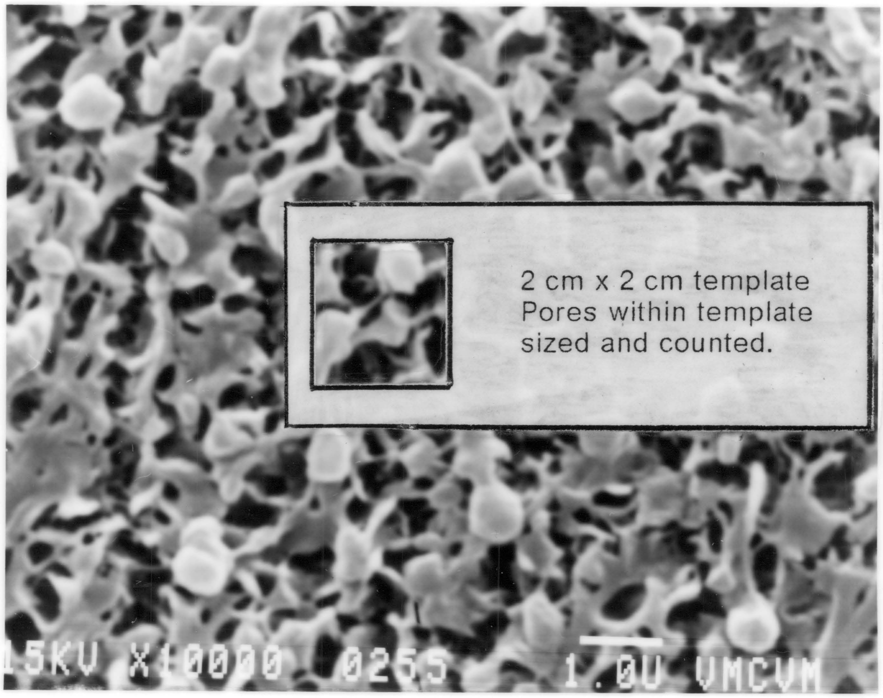

Figure 9. Pore sizing and counting on a typical micrograph.
Magnification: 10,000

Chapter 4

Preliminary Investigation of Process Parameters

Before investigating the quantitative effects of different process parameters on the porous nature of the material produced, qualitative effects of certain parameter changes were investigated. It was determined that for the particular material chosen for this investigation, some of the processing steps could be removed and a porous material still result.

4.1 Material Selection

Initial small-sample experiments had been successful in producing porous materials using an unidentified polyethylene film. Sufficient quantities of this material were not available and the important material properties which made the material useful were not known. Samples of various polyethylene films were obtained from several film manufacturers and evaluated as possible choices for investigation. Small sample pulls in proprietary solution 1 were done on each of the films received. One of these films showed results that were very similar in nature to the unidentified plastic. The material was a 0.004-in. (0.10-mm) thick film made from polyethylene resins. This material was chosen for the investigation.

4.2 Qualitative Effects of Various Process Steps

Experimentation began with the simple scale up of the small sample experiments in solution 1 without the use of a solution 2. Samples of material were drawn using the stretcher at stretch ratios of 2:1, 3:1, and 4:1 in solution 1. Solution temperatures ranging from 75°C to 80°C were tried. Dwell times in the bath ranged from 10 seconds to 1 minute. With each trial, the resulting material was restrained in the clamping frame and allowed to solidify by drying. The materials produced were somewhat cloudy in appearance but would not allow the passage of air in the standard flow test. It was concluded that any pores that were present did not extend through the entire material.

The use of proprietary solution 2 was added to the process to produce material with pores that extended throughout the entire thickness. It was found that when the previously described process was repeated, followed by a subsequent immersion into a heated bath of solution 2, the formation of a completely porous material resulted. Extended experiments were performed with solution 1 at 78°C and a solution 2 at 82°C. The material was stretched 300% at a rate of 20% per second. Total dwell time was 20 seconds in the solution 1 (including the stretch time). Upon removal from the solution, the film was restrained in the clamping frame and immersed in solution 2 for 60 seconds.

The coloration of the material that was produced was varied. In some regions, a uniform silvery white color was present; other regions still had the clear appearance of the untreated film. Gas flow rates through the material under the standard flow test varied substantially from 14 - 130 ml/min. The visual nonuniformity in color seemed to be the result of nonuniform shrinkage and clamp slippage. It was concluded that forces which were introduced into the membrane upon immersion into the second bath would be difficult to uniformly distribute and control. Manufacture of membranes of a predictable nature was not considered likely. It was decided to remove the clamping step from the process and evaluate the material.

Several trials were performed without the use of the clamping step in the process. The trials were performed using a 300% elongation and a 20% per second stretch rate. Temperatures ranging from 75° to 78°C were used in the solution 1 with a total dwell time of 20 seconds. The temperature in solution 2 was 82°C with a dwell time of 60 seconds being used. Flow rates through the material using the standard flow test ranged from 20 to 60 ml/min, with the higher flows being obtained at the higher solution temperatures.

The material had a uniform milky white appearance indicating the uniform development of micropores. A photograph of the typical resulting structure is shown in Fig. 10. Solution 1 was at 76°C during the preparation of this sample. Pore size was determined to range from about 0.1 to 0.3 micron, with an average of 0.18 micron. Pore density was 0.9×10^9 pores/cm^2

It was postulated that a porous material could also be produced without stretching the material in solution 1. Several membranes were processed under conditions as described in the previous section with the exclusion of the 300% stretch in solution 1. The membranes showed no significant differences in the

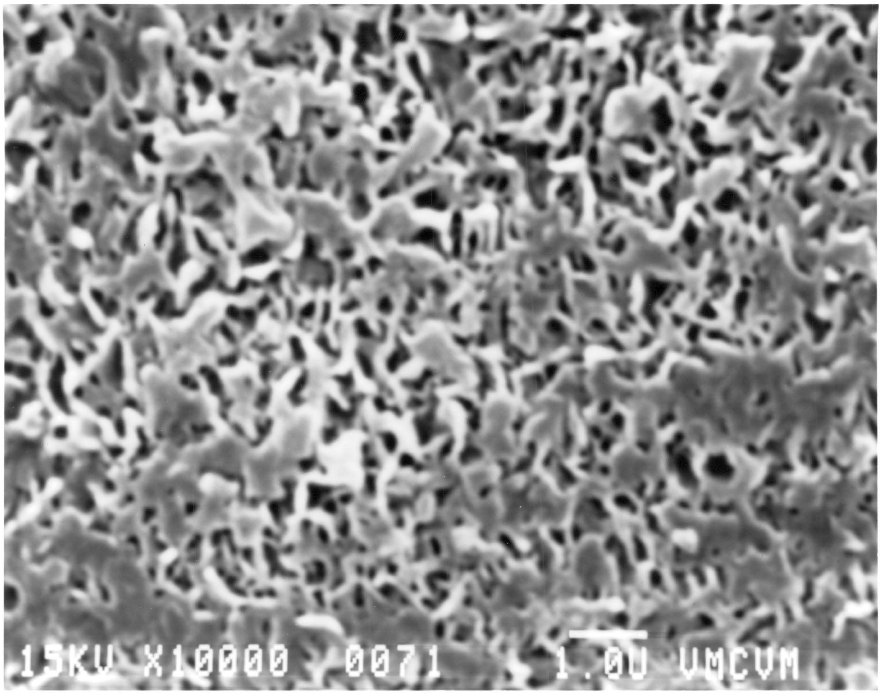

Figure 10. Surface micrograph of porous membrane manufactured with a 3:1 stretch in solution 1, unrestrained in in solution 2.

Solution 1 - Temperature: 74°C Dwell time: 20 sec
Solution 2 - Temperature: 82°C Dwell time: 60 sec
Magnification: 10,000

standard flow test. It was concluded that the inclusion of processing steps such as stretching and clamping did not provide any useful purpose in producing porous films with the specific material used. Table 1 has been included on the following page to review the qualitative results of the effects each processing step was found to have on the porous nature of the material produced. A quantitative investigation into the process with the inclusion of the soak in solution 2 and no stretching or clamping is contained in the following chapter.

Table 1. Qualitative Effects of Changing Various Processing Steps

	MANUFACTURING CONDITIONS					
	SOLUTION 1		SOLUTION 2		PERCENT STRETCH	RESULTS
METHOD OF MANUFACTURE	Temperature (°C)	Dwell Time (sec)	Temperature (°C)	Dwell Time (sec)		
Simple Stretch In Solution 1 Restrained while Setting	75 - 80	10 - 60	-	-	200 - 400 %	Translucent silver color. No Flow in Standard Flow Test. Not Porous Throughout.
Stretch In Solution 1 with Restrained soak In Solution 2	78	20	80	60	300 %	Milky white in color, not uniformly. Membranes Very Unpredictable. Standard Flow Test: 14 - 130 ml/min
Stretch In Solution 1 with Unrestrained Soak In Solution 2	75 - 78	20	80	60	300 %	Uniformly milky white in color. Standard Flow Test: 20 - 60 ml/min Average Pore Size : 0.18 micron Average Pore Density: 0.9 x 10^9 pores/cm^2
Simplified Process - No Stretch Soak In Both Solutions	74 - 78	10 - 60	60 - 78	5 - 60	none	Uniformly milky white in color. Standard Flow Test: 4 - 50 ml/min Average Pore Size : 0.17 micron Average Pore Density : 0.9 x 10^9 pores/cm^2

Chapter 5

Results of Investigation of Simplified Process

In the work described in the previous chapter, the major emphasis was on determining the important process parameters under which uniform porous materials could be produced. Several process variables were able to be removed from the process either because of the problems that they presented or because they had little effect on the nature of the material that was being produced. The elimination of these parameters left only a limited number of variables to be investigated in depth. These included the dwell time and temperature in the solution baths. An investigation into these parameters was undertaken.

5.1 The Effect Of Time and Temperature in Solution 1

Investigations of the effect of varying both time and temperature in solution 1 on the porous nature of the material produced were conducted. Solution 1 temperatures were varied from 70°C to 80°C in increments of 2°C. At each temperature, dwell time in the solution was varied from 5 to 40 seconds. Testable material was not produced under all of the conditions that were tried. At temperatures of 80°C and above, the material became almost liquid and could not be wholly transferred into solution bath 2. This same phenomenon was found to result after a 30 second dwell time in solution 1 when the bath was at 78°C. At temperatures of 72°C and below, the material produced would not permit the passage of air in the standard flow test.

Membranes of a testable nature were able to be produced when solution 1 was at temperatures of 74°C, 76°C and 78°C. The results of the standard flow test for various solution 1 temperatures and dwell times tried are shown in Table 2. The highest, lowest and mean flow rates of the four membranes tested are in this table. A plot of dwell time versus the results of the standard flow test for various solution temperatures is shown in Fig. 11.

The results show that the rate of air permeation through the membrane is strongly dependant on the manufacturing temperature in solution 1. When a dwell time of 30 seconds was used, a 2°C temperature increase from 74°C to 76°C was found to increase the rate of air permeation through the membrane by 530%. The effect of dwell time, especially at the lower temperatures, was not nearly as great. After a minimum dwell time, extra dwell time used during manufacture no longer had an effect on the rate of air permeation through the membrane. This is most evident in the results of trials run with a temperature of 74°C. No gas flow through the membrane was found to occur when dwell times of 10 seconds and below were tried. When soak times of 20 seconds and above were tried, the resultant membranes had a relatively constant flow rate of about 4.6 ml/min.

The rate of air permeation in the membranes produced under the same conditions was found to vary up to 40% from the mean. The sample-to-sample variation can be attributed to small temperature fluctuations that occurred in solution 1 during

Table 2. Results of Time-Temperature Studies in Solution 1

Solution 1		Results of Standard Flow Test		
Temperature (°C)	Dwell Time (sec)	High Flow Rate (ml/min)	Low Flow Rate (ml/min)	Mean Flow Rate (ml/min)
78	5	0.0	0.0	0.0
78	10	13	4.7	8.3
78	20	46	35	40
78	30	49	38	45
76	10	8.8	4.8	6.5
76	20	24	14	21
76	30	39	25	31
76	40	45	25	36
74	10	0.0	0.0	0.0
74	20	5.9	3.0	4.2
74	30	6.7	2.7	4.9
74	40	5.8	3.9	4.6
74	50	6.1	3.8	4.9

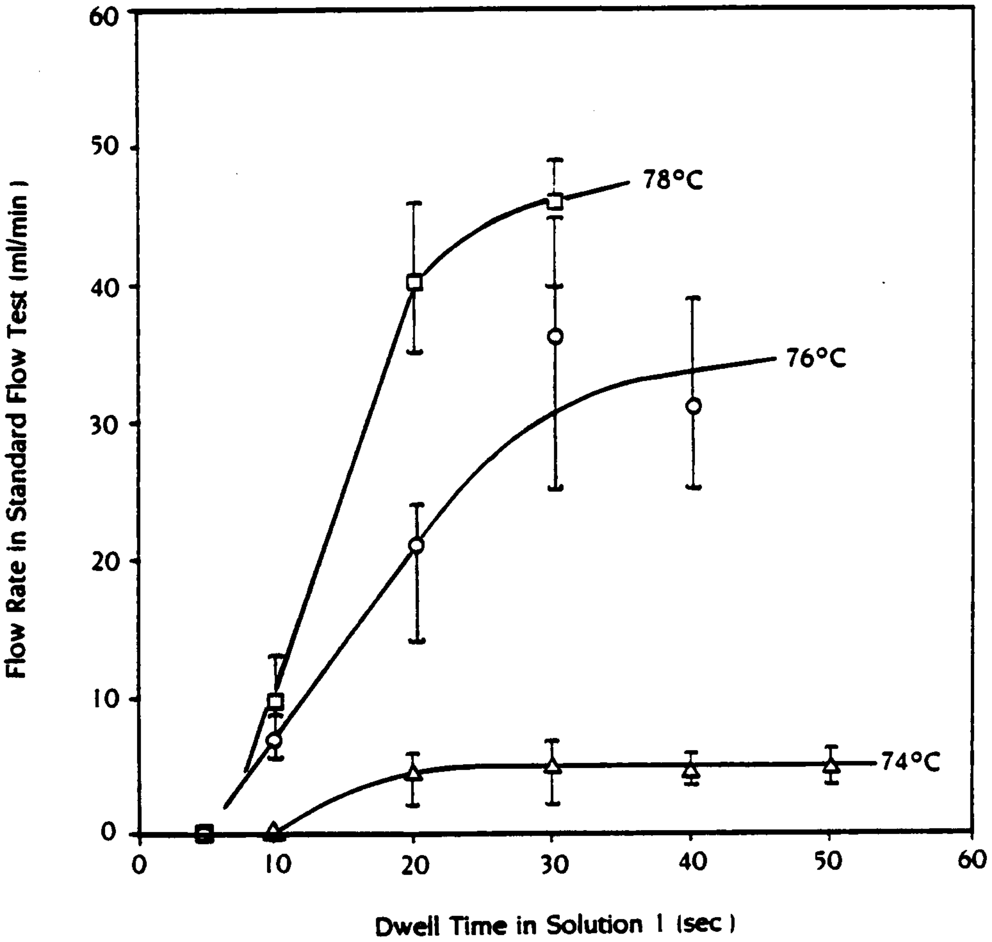

Figure 11. Plot of solution 1 dwell time vs flow rate in the standard flow test for various solution 1 temperatures.

the manufacture of the samples. The solution 1 temperature uncertainty was ± 1°C which is sufficient to explain the resultant variability.

With extended soak times, porous material was produced with a solution 1 temperature of 72°C. When a dwell time of 3 minutes in the solution was employed, porous membranes that allowed an average flow of 1.7 ml/min in the standard flow test were produced. The appearance of the material was more translucent than the material produced under the previously described conditions.

Samples were selected from the produced membranes to be viewed under the scanning electron microscope in order to determine the cause of the changes in the rate of air permeation through the membrane. Examination of these materials gave insight into the reasons for the changes that occurred in the membrane's flow characteristics. Membranes produced at 76°C and 78°C were highly nonuniform in structure when viewed with the scanning electron microscope. A great variety of structural features were present, with some areas being virtually devoid of pores and other areas being riddled with cracks and voids of various sizes. It was not possible to locate and photograph an area that was representative of the structure of the material produced.

Figure 12 is a photomicrograph of a fairly representative area of the membrane structure where some uniformity was present. The particular membrane which was photographed was produced using a 20-second dwell time in solution 1 at a temperature of 76°C. Average pore size in this region was 0.15 micron and pore density, 0.7×10^9 pores/cm^2.

Membranes produced with a solution 1 temperature of 74°C had a very uniform structure. Photomicrographs that were taken of the membrane surface and cross section were representative of the structure that was present in the material. Figure 13 is a photomicrograph of the typical surface structure that is produced with a solution 1 bath temperature of 74°C. The magnification is 2,000 so that the uni-

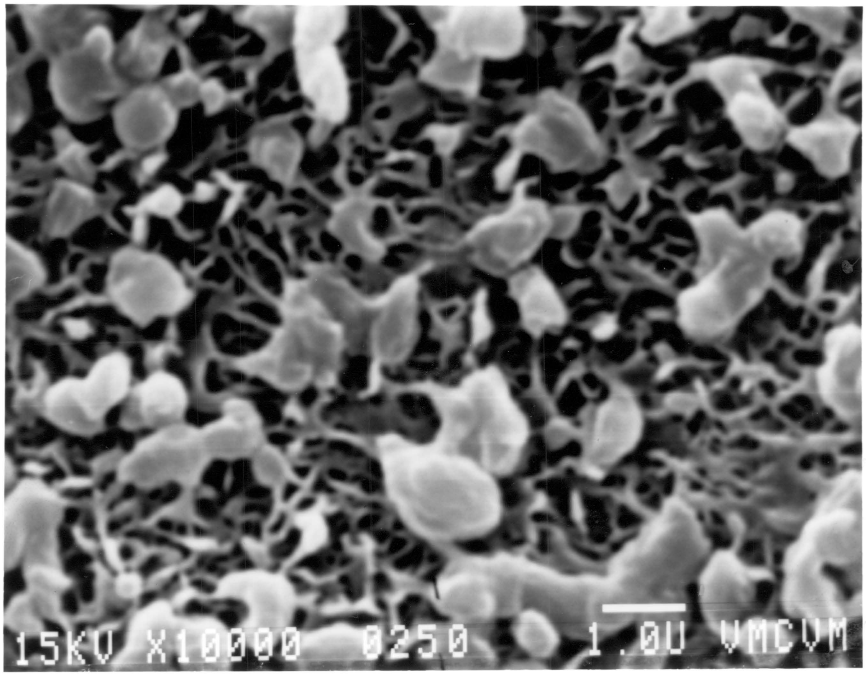

Figure 12. Surface micrograph of a uniform region in a membrane produced with a solution 1 temperature of 76°C.

Solution 1 - Temperature: 76°C Dwell time: 20 sec
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 10,000

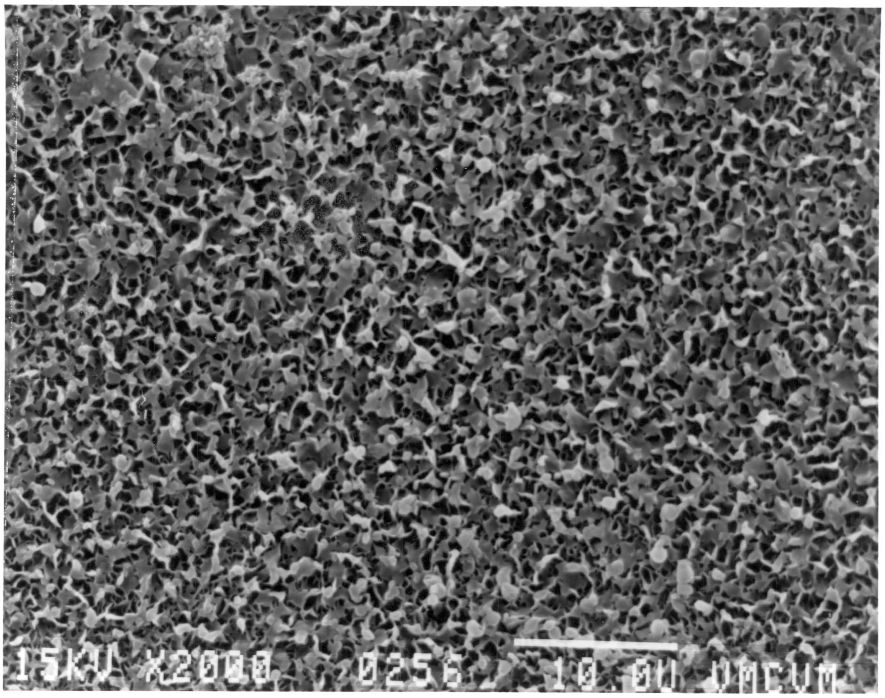

Figure 13. Low magnification surface micrograph of membrane produced with a solution 1 temperature of 74° C.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 2,000

formity in the porous structure can be seen. Figure 14 is a photomicrograph of the typical structure that results under these same conditions but at a magnification of 10,000 so that the pore structure can be viewed. The pores were found to range in size from about 0.1 to 0.3 micron with the average being 0.17 micron. The average pore density was 0.9 x 10^9 pores/cm^2.

Figure 15 is a photomicrograph of a typical complete cross section of the material produced using a solution 1 bath temperature of 74°C. The structure which is present can be seen to extend uniformly throughout the membrane. Figure 16 is a high magnification photograph of the same cross section. It is noticeably different from the surface topography. The combination of the high magnification views of both the surface and the cross section indicate the existence of a sponge-like structure with small tortuous paths between one surface and the other.

Surface micrographs were also taken of the material produced with a 3-min soak time in solution 1 at a temperature of 72°C. Figure 17 is a typical photomicrograph of the surface. Pore size in this material was found to range from about 0.1 to 0.2 micron with an average of 0.11 micron. Pore density was found to average 0.6 x 10^9 pores/cm^2. In comparison to the membranes produced using a 74°C solution 1 temperature, the pore density has decreased by 33% and the average pore size decreased by 35%.

5.2 Effect of Temperature and Dwell Time in Solution 2

Results of the temperature and time studies in solution 1 indicated that the best uniformity of pore structure was obtained when a 74°C solution 1 temperature was used with a solution dwell time of 20 seconds or longer. During the investi-

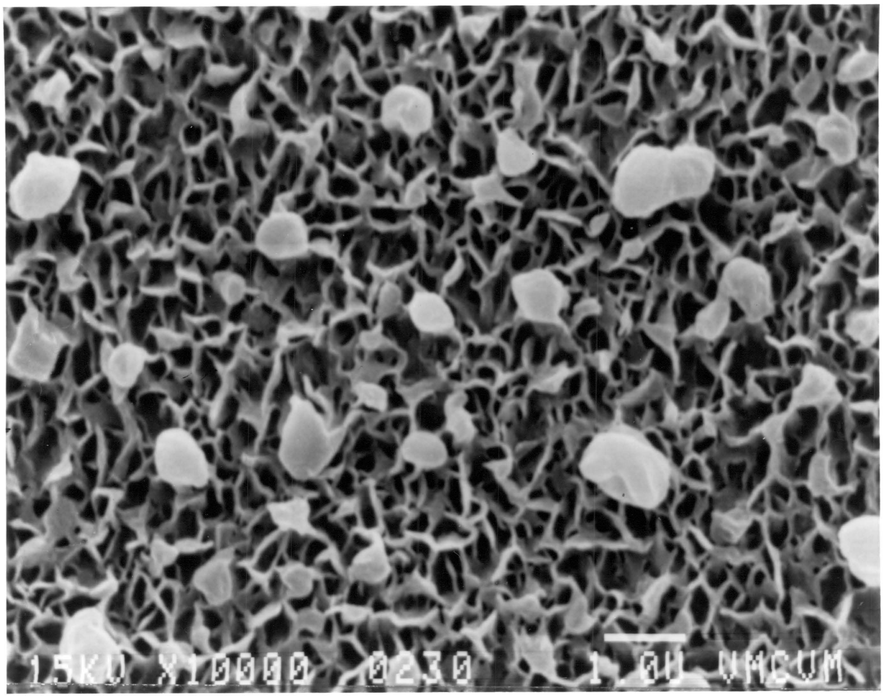

Figure 14. Surface micrograph of membrane produced with a solution 1 temperature of 74°C.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 10,000

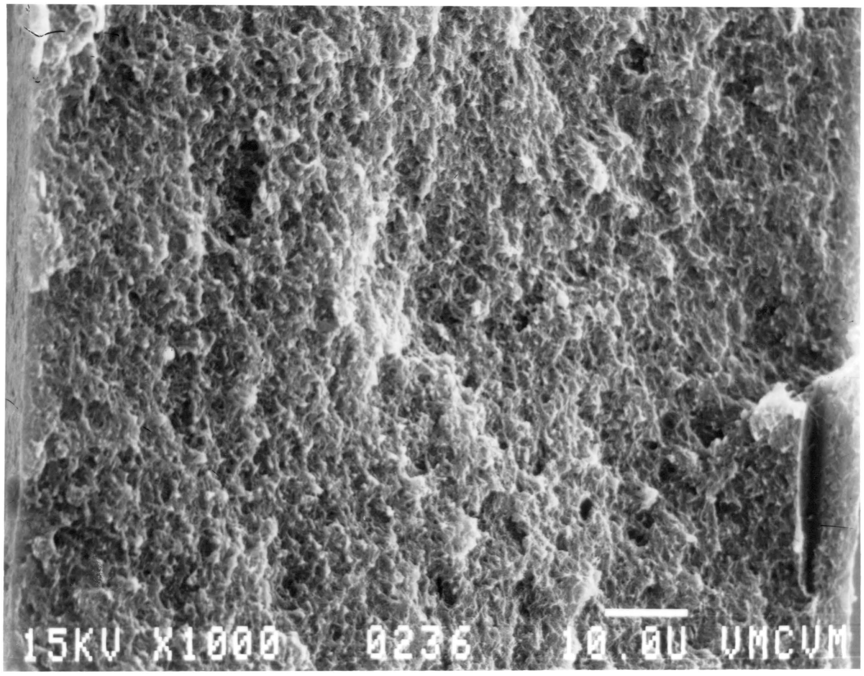

Figure 15. Micrograph of complete cross-section of membrane produced with a solution 1 temperature of 74°C.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 1,000

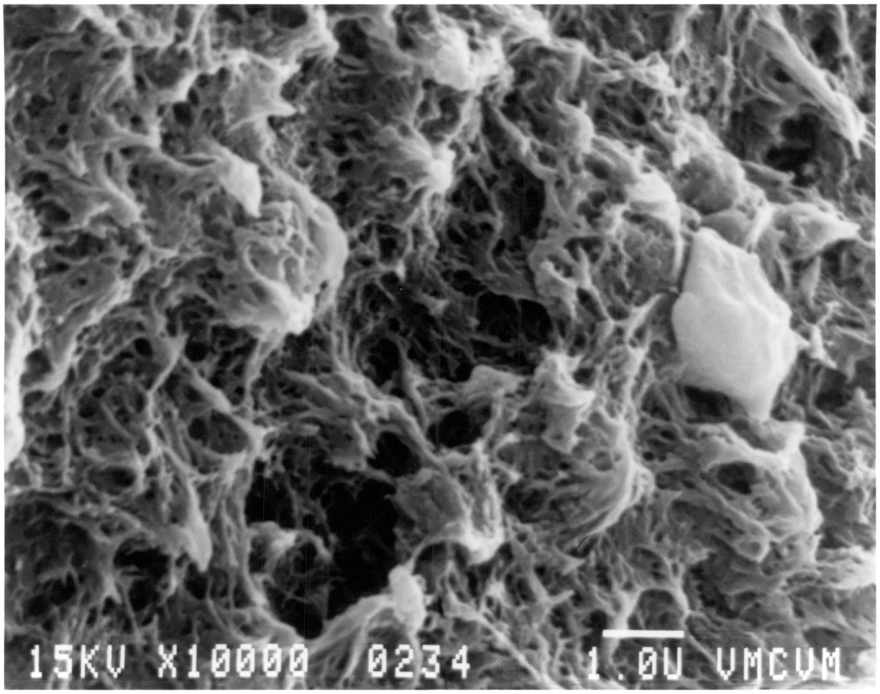

Figure 16. Micrograph of cross-section of membrane produced with a solution 1 temperature of 74°C.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 10,000

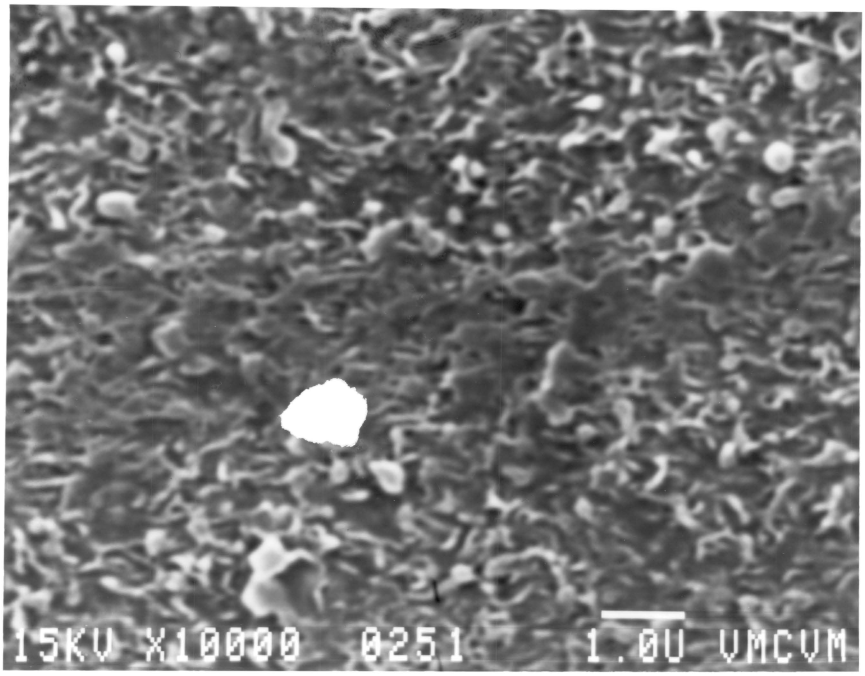

Figure 17. Surface micrograph of membrane produced with a solution 1 temperature of 72°C.

Solution 1 - Temperature: 72°C Dwell time: 3 min
Solution 2 - Temperature: 74°C Dwell time: 60 sec
Magnification: 10,000

gations, solution 2 was kept at a constant temperature of 74°C. Dwell time in the solution was kept constant at 60 seconds. Investigations were then conducted into the effect of varying the temperature and dwell time in solution 2 on the porous nature of the material produced. Throughout these experiments, the temperature in solution 1 was kept constant at 74°C; dwell time was kept constant at 30 seconds.

The porous nature of the material produced with a 74°C solution 2 temperature and a 60-second dwell time had already been established in the previous experiments. Membranes were then produced using solution 2 temperatures 4°C higher and lower using this same dwell time. The variation in temperature was continued on the low end in decrements of 5°C, until material of a uniform cloudy appearance was no longer produced. This occurred at a temperature of 60°C. All of the membranes produced were evaluated in the standard flow test. A description of the solution 2 conditions under which membranes were produced, and the results of the standard flow test, are shown in Table 3. A plot of the temperature used in solution 2 versus the results of the gas flow test is shown in Fig. 18. The variability in the results was as high as 40%, but, as before, can be attributed to slight variations in the temperature of solution 1.

The results show that when solution 2 was in a temperature range of 65 to 78°C, the membranes produced had no significant differences in the standard flow test. This indicates that temperature variations in this range do not significantly alter the porous nature of the material produced. The nature of this pore structure had already been established in photomicrographs taken of the material produced with a 74°C solution 2 temperature. This structure is shown in Fig. 14 on page 44. The material that was produced using a solution 2 temperature of 60°C would not allow the passage of air in the standard flow test. A solution 2 temperature of 65°C would appear to be the minimum under which porous material can be expected to be produced.

Table 3. Results of Time & Temperature Studies in Solution 2

Solution 2		Results of Standard Flow Test		
Temperature (°C)	Dwell Time (sec)	High Flow Rate (ml/min)	Low Flow Rate (ml/min)	Mean Flow Rate (ml/min)
60	60	0.0	0.0	0.0
65	60	5.9	2.3	4.1
70	60	8.0	3.0	4.9
74	60	6.7	2.7	4.9
78	60	5.0	2.6	3.9
74	3	0.0	0.0	0.0
74	5	4.6	8.1	6.5

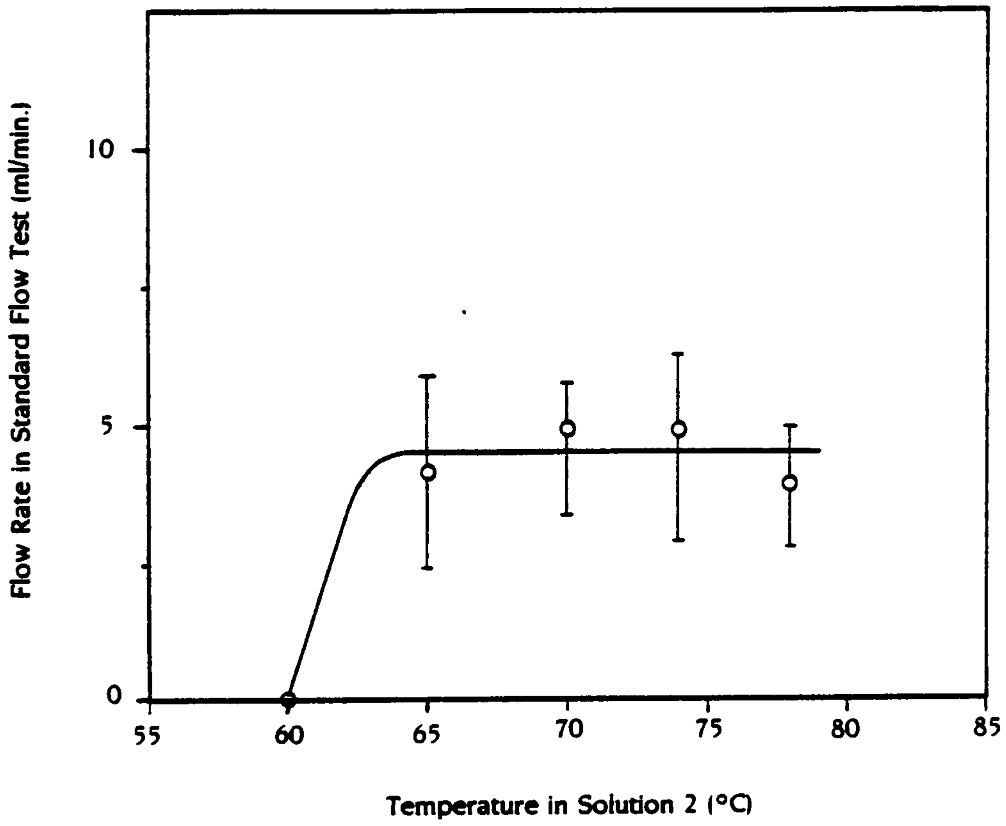

Figure 18. Plot of solution 2 temperature vs flow rate in the standard flow test.

Visual observations of the process indicated that clouding of the material upon immersion into solution 2 occurred after a very short period of time. It was thought that after this initial clouding of the material was complete, continued dwell time in the solution did not have any effect on the porous structure that was produced. With solution 1 conditions kept constant, membranes were produced using a solution 2 temperature of 74°C and dwell times of 3 and 5 seconds. The membranes which were produced after a 3 second dwell time in the solution did not have a uniform milky white color and no detectable gas flow was measured in the standard flow test. Those produced after 5 seconds in solution had a uniform milky white coloration and a flow rate through the material was determined in the standard flow test. The conditions in solution 2 along with the with the results of the standard flow test have been included in table 3.

The membranes produced with a 5-second dwell time had flow rates in the standard flow test ranging from 4.6 to 8.1 ml/min with a mean of 6.3 ml/min. This mean flow rate is slightly higher than the mean flow rate obtained on membranes produced under similar conditions, but with a solution 2 dwell time of 60 seconds. With variability caused by temperature variations in solution 1 being as high as 40%, the observed difference is not significant.

The surface and cross section of partially clouded regions in the membranes produced after a 3-second dwell time in solution 2 were examined using the scanning electron microscope. Photomicrographs of the structure are shown in Figs. 19 through 21. The material structure is not microporous. There appears to be a critical time of 5 seconds in solution 2 needed in order to produce material that is microporous. Beyond this initiation time, the porous structure cannot be expected to be significantly altered by changes in the dwell time.

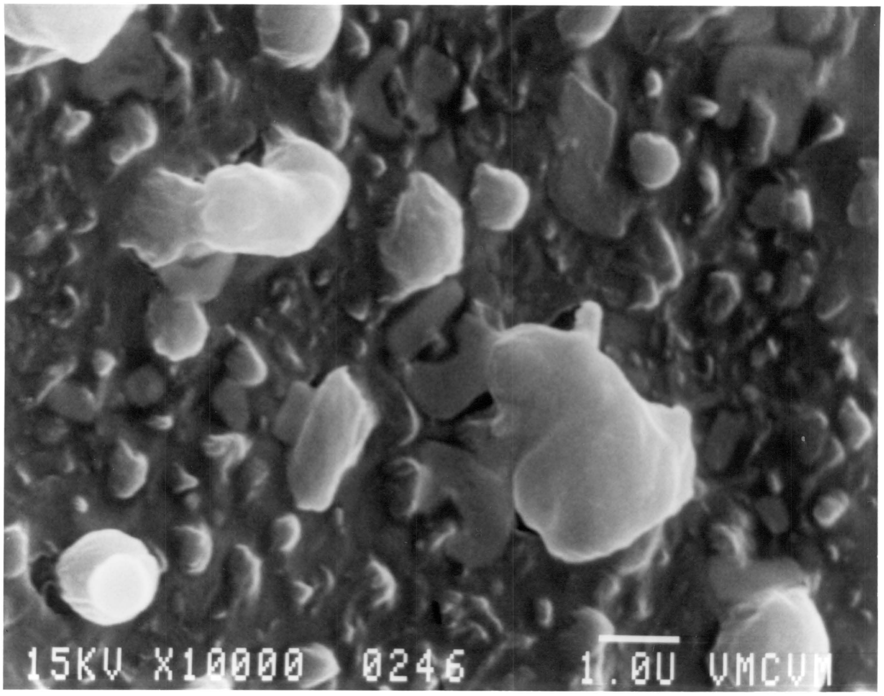

Figure 19. Surface micrograph of material produced with an insufficient dwell time in solution 2.

Solution 1 - Temperature: 74°C Dwell time: 30 sec
Solution 2 - Temperature: 74°C Dwell time: 3 sec
Magnification: 10,000

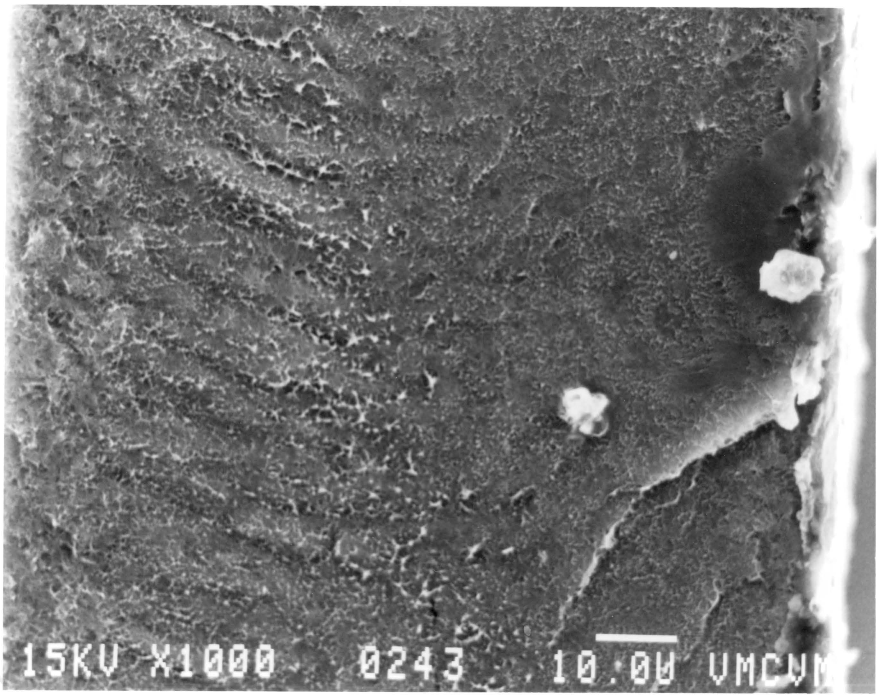

Figure 20. Micrograph of complete cross-section of the material produced with insufficient dwell time in solution 2.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 3 sec
Magnification: 1,000

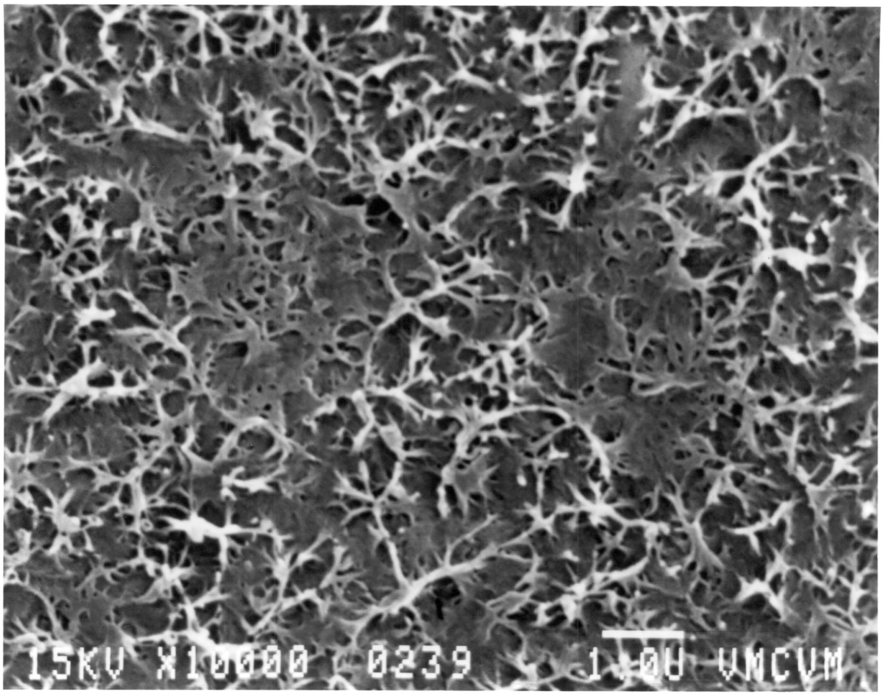

Figure 21. Micrograph of cross-section of the material produced with insufficient dwell time in solution 2.

Solution 1 - Temperature: 74°C Dwell time: 40 sec
Solution 2 - Temperature: 74°C Dwell time: 3 sec
Magnification: 10,000

5.3 *Effect of Cold Drawing After Manufacture*

Several membranes were manufactured using a 30-second dwell time in solution 1 at 74°C and a 60-second dwell time in solution 2 at 74°C. After these membranes had dried, they were biaxially cold drawn using the stretcher. The membrane was elongated 170% in one direction at a rate of 17% per second. Upon completion of the stretching, the membrane was held restrained in its elongated state for a period of 1 minute. Upon release the membrane relaxed back to 114% of its original length. This same procedure was repeated in the remaining direction to yield a biaxially stretched membrane.

The resulting material showed flow rates in the standard flow test ranging from 57 to 100 ml/min. The feel of the material had been significantly altered. The rather stiff material had taken on an almost cloth like feel. Examination under the scanning electron microscope revealed that the stretching had introduced a network of discontinuities that appeared as surface cracks in the already porous structure. Figure 22 is a photomicrograph of the membrane surface showing the structure that was present. A high magnification photomicrograph, as shown in Fig. 23, revealed that these apparent cracks did not extend through the material. The crack regions, as outlined in Fig. 23, were areas were the average pore diameter had been increaed in size significantly over that of the surrounding area. The pore size in these regions, was found to range from 0.1 to 0.5 micron with an average of 0.27 micron. The average pore density was 0.4 x 10^9 pores/cm^2. This is a 50% increase in average pore size over that in the surrounding material. A 55% decrease in pore density accompanied this change.

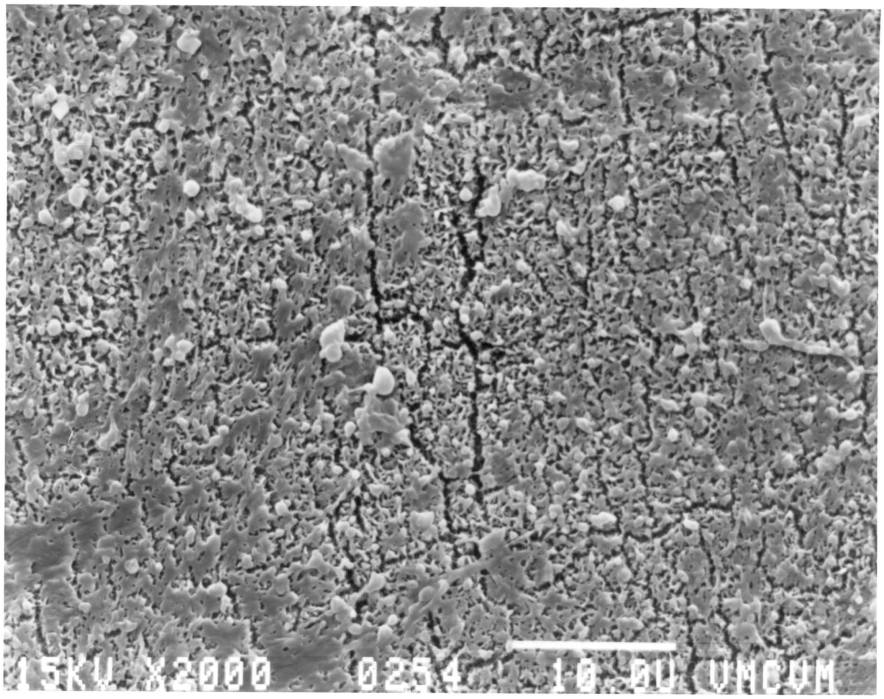

Figure 22. Surface micrograph of a cold drawn membrane showing apparent surface cracks in membrane structure. Magnification: 2,000

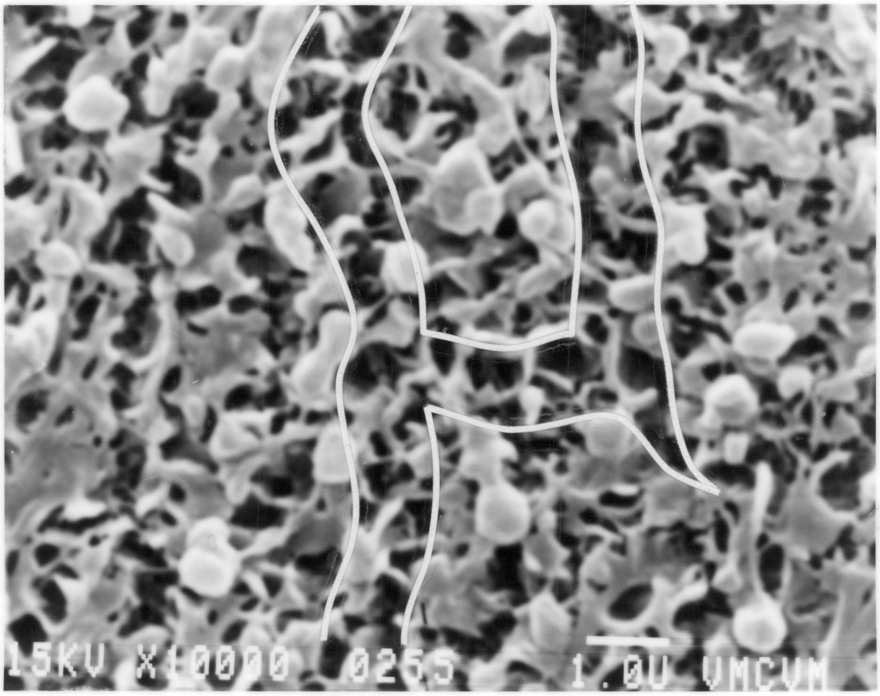

Figure 23. Surface micrograph of a cold drawn membrane showing pore structure within apparent surface cracks. Approximate crack outlines shown in white. Magnification: 10,000

Chapter 6

The Testing of Mechanical Properties

It was of interest to determine the overall effect of the process on the yield point, ultimate strength, and elongation at break in the material produced. This information was desired in order to determine the strength limitations that would be imposed by the material in various applications.

6.1 Testing Procedure

The mechanical properties were tested using an Instron model 1122 universal testing instrument. This is a constant-rate-of-cross-head-movement-type testing machine with instrumented heads for force measurements. Dog-bone shaped samples of material were prepared with a test section 2.8 mm wide and 10 mm long using a die and hand press as shown in Fig. 24. The thickness of the samples were measured using a snap gauge to the nearest 0.5 mil (0.013 mm). Samples were clamped

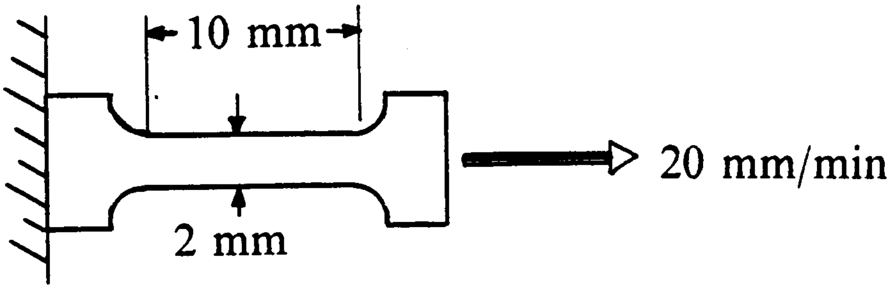

Figure 24. Sample dimensions used for mechanical testing.

between the cross heads of the machine and drawn at a constant rate. A rate of cross head movement was chosen that would rupture the sample within a 0.5 to 5 minute time period as suggested in ASTM standard D638. A rate of 20 mm/min was found to give a rupture time between 2 to 3 minutes for the samples that were to be tested and was therefore selected. During the extension of the sample, the induced force was recorded on strip chart moving at a constant speed.

6.2 Results of Mechanical Testing

Mechanical properties in four different samples were tested in mutually perpendicular directions in both the raw film and the porous films prepared. The porous films were prepared using a solution 1 temperature of 74°C and a 30 second solution dwell time. A temperature of 74°C and a dwell time of 60 seconds were used in solution 2.

The resulting strip charts produced during testing were too long to be included within this thesis. A representation of the form which resulted is shown in Fig. 25. During the initial stages of drawing, there was a steep linear increase in measured force with elongation. The point of deviation from this linearity was taken as the yield point. After this region of linearity, a slow nonlinear increase in measured force continued. After reaching a maximum, the material then slowly pulled apart to failure. The maximum measured force was used in the calculation of the ultimate strength. The elongation at the point of final failure was used in the determination of the percent elongation at break. The material properties determined were based on the outside dimensions of the samples before testing. No attempt was made to account

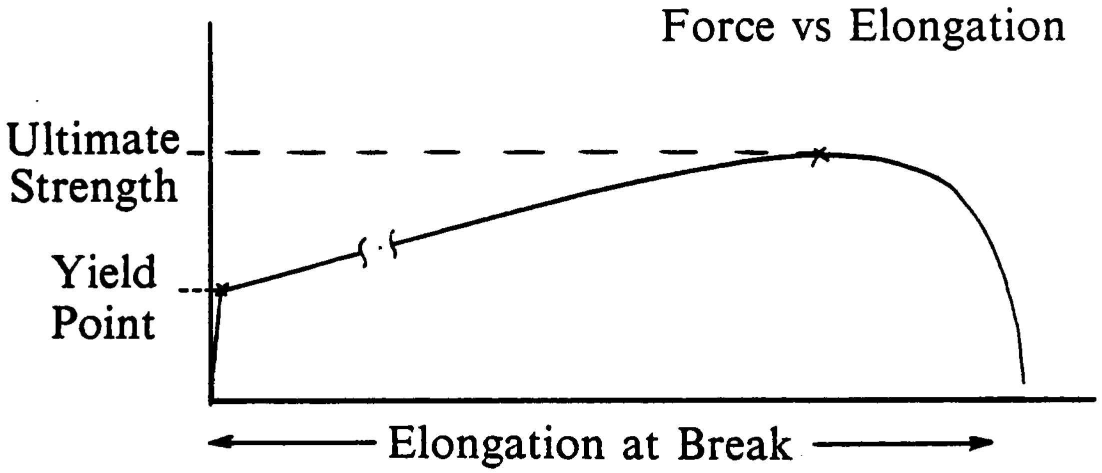

Figure 25. Basic form of force vs elongation plots on both porous and nonporous polyethylene.

for the porosity of the material or the necking which occurred during the drawing of the material.

The results of the strength tests are presented in Table 4. They indicate that the generation of the porous structure resulted in a 50 - 65% reduction in both the yield point and ultimate strength of the material. The elongation at break was reduced from 560-580% to 360-420%.

This reduction in mechanical strength in the material is not surprising. In the processing of the membrane, the generation of the porous structure has resulted in the reduction of the real cross-sectional area of the membrane. Since no attempt was made to correct for this loss in cross-sectional area a decrease in the mechanical strength should be expected. It should be noted, that the presentation of the mechanical strength based on the outside dimensions of the material, would be the required value when attempting to size a membrane's thickness for specific strength requirements.

Table 4. Results of Mechanical Testing of Porous and Nonporous Films

Direction	Property	Initial Film	Processed Film	% Change
1	Yield Point	1,330 psi (9.2 MPa)	840 psi (5.8 MPa)	-63%
	Ultimate Strength	2,840 psi (19.6 MPa)	1,260 psi (8.7 MPa)	-55%
	Elongation at Break	580%	420%	-27%
2	Yield Point	1,220 psi (8.4 MPa)	610 psi (4.2 MPa)	-50%
	Ultimate Strength	2,900 psi (20.0 MPa)	1,070 psi (7.4 MPa)	-63%
	Elongation at Break	560%	360%	-36%

Processed film was treated first with solution 1 at a temperature of 74°C for 30 sec. It was then treated with solution 2 at a temperature of 74°C for 60 sec and dried before testing.

Chapter 7

Discussion and Conclusions

It was the goal of this research to determine the effects of changing process parameters on the porous nature of the material produced from a new proprietary process for the manufacture of microporous polyethylene. It was determined that for the particular polyethylene used, the effect of some processing steps was to introduce nonuniformity without providing significant changes in the membrane structure. The stretching and restraining of the material both were eliminated from the process.

The temperature and dwell time in solution 1 were found to be the most critical factors in determining the nature of the material produced. Porous membranes were producible only in a range of 72 to 78°C. The nature of the material produced was strongly related to the temperature in this solution. Variations of 2°C were found to greatly influence the nature of the material produced. Time and temperature variations did not appear to be a useful method for the modification of pore size and distribution. When temperatures were increased in the range of 74 to 78°C an increase in the pore size did not occur; instead, increased open area was introduced in a nonuniform fashion. This resulted in higher gas flow rates through the membranes. Temperatures below 74°C did provide a means for decreasing the resulting pore size, but production of membranes under these conditions required extended dwell times.

Membranes produced at 74°C were by far the best in uniformity of structure and flow characteristics. Bath dwell time was found to have no major effect when increased beyond 20 seconds. Membranes produced had a uniform milky white coloration and a velvet-like feel. Pores were fairly uniform in size averaging 0.17 micron and pore density was 0.9×10^9 pores/cm^2. The generation of this porous structure was found to result in a decrease in the yield point and ultimate strength of the original film by 50 - 65%. The yield point of the material, based on the measured outside dimensions prior to testing was 610 - 840 psi (4.2 - 5.8 MPa).

The use of solution bath 2 was found to be critical for the manufacture of porous material, though the conditions used did not greatly effect the structure. It was determined that beyond a critical temperature of about 65°C, porous material resulted and increases in temperature did not significantly change membrane properties. Similarly, it was found that beyond a critical dwell time of about 5 seconds, porous material resulted and further increases in dwell time did not result in significant changes to the membrane properties.

Cold drawing of the material after manufacture was found to give the material a more cloth-like feel and appearance. An increase in the gas flow rate through the membranes also resulted. Apparent surface cracks were present in the structure which resulted. Closer examination showed these areas to be regions where pore size had been significantly increased with no cracks extending through the structure. Further investigation into the use of this approach to increase pore size was not performed in this investigation. It may be possible to uniformly open up the pore structure through the use of different stretch rates, ratios and temperatures. This should be a point for further investigation.

For all of the parameters investigated, no practical means of uniform control of pore size was determined. Variations in the parameters investigated resulted in the introduction of nonuniformity or had no effect on the porous nature of the material produced. The effect of modification of the base film composition was not investigated and could be a parameter that would provide the desired control over pore characteristics. Further investigation into this is needed.

Through this investigation, the determination of the effects of changing process parameters has aided in the understanding of the conditions under which an industrial process might operate. Additionally, insight into the needed control requirements for a process of this type has been gained. It is believed that the information obtained in this research should aid in the commercialization and application of this process.

Chapter 8

Recommendations

1. The temperature-controlled bath developed to control the temperature in solution 1 did not provide the needed control required to manufacture membranes with a high repeatability. If future work is to include the use of this piece of equipment, several modifications should be made. These should include:

   a. Insulation of the outer bath to reduce thermal losses from the system.

   b. The use of a heat transfer fluid with a higher thermal conductivity and boiling point in the outer bath.

   c. Implementation of a more precise temperature controller which should include the use of a thermocouple or a thermistor as a means of temperature sensing.

2. The experiments that were performed in this research were done using a batch-type process. Any industrial process using the techniques investigated would

operate in a continuous mode. Future work should include the development of equipment that would process material in a similar way. The use of continuous processing equipment would also eliminate problems associated with the transfer of materials between the solution baths.

3. The work conducted in this research was empirical by nature and specific chemical models which could be used to describe the state of the material throughout the process were not developed. Chemical engineering work directed at developing models for the process mechanisms could provide further useful information for commercialization and application of the process.

4. No means of pore size and pore density control was determined in the investigation. Further experimentation should concentrate on methods by which this can be accomplished. Two methods of approach which may prove fruitful are (i) The use of polyethylene films with different material compositions in the process and (ii) The use of post stretching of the material after processing at various ratios, rates and temperatures.

5. Experimentation into the effect of process variables on the mechanical properties of the material produced from the process should be more completely investigated. Membranes produced under different processing conditions should be tested. Only the mechanical properties which resulted in the material produced under one specific set of conditions was investigated in this research.

6. Evaluation of the material produced centered around air flow measurements and examination under the scanning electron microscope in this research. Other membrane properties such as moisture vapor transmission rate, porosity, critical surface tension, and material Gurley number have not been determined for the

material. These are properties which require the use of specialized equipment which was not available during this investigation. It may be of value to determine these properties for material which was produced from the process, and investigate the effects of process parameters on each property.

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