Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Chaiko, David J. and Osseo-asare, K.(1982) 'Characterization of Liquid Membrane Supports', Separation Science and Technology, 17: 15, 1659 — 1679
To link to this Article: DOI: 10.1080/01496398208055649
URL: http://dx.doi.org/10.1080/01496398208055649

SEPARATION SCIENCE AND TECHNOLOGY, 17(15), pp. 1659–1679, 1982-83

Characterization of Liquid Membrane Supports

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Abstract

Two polypropylene films, Celgard 2400 and Celgard 2500 (products of Celanese Corp.), were examined by scanning electron microscopy before and after impregnation with a 0.2 kmol/m^3 dodecane solution of dinonylnaphthalene sulfonic acid for 55 d. In the photomicrographs of the untreated film samples, the surface pores appeared as a regular pattern of slots. Mercury porosimetry results indicate that the pores are present as a very narrow size distribution: 0.01 μm < 90% < 0.062 μm. The photomicrographs of the treated film samples showed an extensive loss of porosity.

INTRODUCTION

A microporous film must be resistant to attack by strong acids, bases, and organic solvents if it is to function successfully as a liquid membrane support. Presently, the literature contains very little information concerning the ability of membrane supports to maintain their integrity and porous structure under extended liquid membrane extraction conditions. Largman and Sifniades (*1*) reported that structural changes occurred in a Gore-Tex film when it was impregnated with a LIX 64N-kerosene solution and operated in an extraction mode for several days. The authors reported differences between membranes which were (a) untreated, (b) freshly impregnated with a LIX 64N-kerosene solution, and (c) impregnated with a LIX 64N-kerosene solution and operated as a liquid membrane for several days. However, the nature of these differences was not described.

This paper reports results obtained as part of a continuing study aimed at developing Accelerated Coupled Transport Systems (ACTS) for use in the liquid membrane recovery of metals (*2, 3*). Two microporous polypropylene films utilized in a study of cobalt transport across dinonylnaphthalene sulfonic acid (HDNNS) liquid membranes were examined by scanning electron microscopy (SEM) before and after treatment with an organic HDNNS solution. In addition, pore size distributions were determined by mercury porosimetry.

EXPERIMENTAL METHODS

Reagents and Materials

HDNNS was supplied by King Industries Inc. and purified as previously reported (*4*). Dodecane and hexane were Fisher certified reagents. SPURRS epoxy resin, used in the preparation of thin sections, was purchased from LADD Research Inc. The two membrane support films used in this study were Celgard 2400 and 2500. Both films are manufactured by Celanese Corp.

Preparation of Membrane Support Films for SEM Study

For the SEM investigations, samples of Celgard 2400 and Celgard 2500 were obtained in three ways: (a) Pieces cut from an untreated roll of film received from the manufacturer were mounted on metal studs and gold coated. Both face and edge view samples were prepared in this manner. (b) Samples of Celgard 2400 were soaked in a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d. Face and edge view samples of the impregnated material were prepared by first washing with ethanol to remove the impregnated organic phase, followed by mounting on metal studs and gold coating. (c) Thin sections were prepared directly from the impregnated film pieces as described below.

Preparation of Thin Sections for SEM Study

Several pieces of Celgard 2400 film were soaked in a 0.2 kmol/m^3 HDNNS–dodecane solution for approximately 55 d. Prior to thin sectioning, the film samples were immersed overnight in a solution containing 75%

dodecane and 25% epoxy resin (SPURRS). The resin content was increased from 25 to 50%, 75%, and 100% over four consecutive days. This procedure, as suggested by the film manufacturer (*5*), was followed with the hope of getting a representative view of the membrane as it appears when impregnated with a dodecane solution of HDNNS. All samples were gold coated prior to viewing by SEM.

Mercury Porosimetry

Several samples of Celgard 2400 were soaked in 0.2 kmol/m^3 HDNNS–dodecane for varying lengths of time. Upon removal from the HDNNS solution, the film samples were rinsed and then soaked in hexane. The hexane was exchanged for fresh hexane at about 5 min intervals for a total of about 30 min. The samples were dried and pore size distributions were measured by a mercury intrusion method using a Quantachrome Scanning Porosimeter (Quantachrome Corp.).

The volume of mercury intruded into the membrane pores was measured as a function of pressure. By assuming cylindrical pores, the pore radius can be calculated as follows (*6*):

$$r_p = \frac{2\gamma \cos \theta}{P} \tag{1}$$

where P is the applied pressure, γ is the surface tension of mercury, and θ is the wetting angle for mercury on polypropylene—taken to be 2.443 rad (*7*). The maximum applied pressure was 351.5 kPa and corresponds to a minimum pore radius of 0.0021 μm measurable by this technique.

EXPERIMENTAL RESULTS

Physical Characteristics of Support Films

The Celgard 2000 series are hydrophobic polypropylene films which contain a regular pattern of submicron pores. The films are readily wetted by organic liquids with surface tensions less than 35 mN/m. They are highly resistant to attack by sulfuric acid but swell slightly when contacted with kerosene or other hydrocarbons (*8*). The physical characteristics of Celgard 2400 and 2500, as supplied by the manufacturer, are listed in Table 1.

TABLE 1

Characteristics of Celgard Films[a]

Property	Celgard 2400	Celgard 2500
Thickness	25 μm	25 μm
Porosity	38%	45%
Pore size	0.02 μm	0.04 μm
Critical surface tension	35 mN/m	35 mN/m

[a]Information supplied by Celanese Corp. *(8)*.

The swelling characteristics of Celgard 2400 and 2500 were determined by measuring the change in film length and width after being immersed for 7 d in either dodecane or a 0.20 kmol/m^3 HDNNS–dodecane solution. In all cases an immediate swelling of approximately 1% occurred, after which the films remained dimensionally stable for the 7-d test period.

Photomicrographs of the Support Films

Photomicrographs of Celgard 2400 and 2500, obtained by SEM, are presented in Figs. 1 through 14. Face views of the untreated film samples are presented in Figs. 1 through 4. Figures 5 through 8 are face views of Celgard 2400 samples that had been soaked in a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d prior to microscopy. The photomicrographs in Figs. 1 and 2 were obtained with a slight tilting of the sample stage for increased contrast.

Edge views of untreated samples of Celgard 2400 are shown in Figs. 9 through 11. These are uncut edges obtained from the manufacturer supplied film. Figure 11 clearly illustrates the complexity of the internal pore structure. If the pore structure of Fig. 11 is indicative of the internal pore structure, then it can be seen by comparison of Figs. 11 and 12 that the internal pores are considerably larger than the pores on the front surface.

All photomicrographs of film edges which were exposed by cutting with a sharp knife showed an almost complete loss of pore structure regardless of whether the film was soaked in an HDNNS solution or not. Figure 13 shows a typical cut edge.

Figure 14 is an edge view of a Celgard 2400 sample that had been soaked in a 0.2 kmol/m^3 HDNNS–dodecane solution and subsequently prepared as a thin section. Photomicrographs at magnifications as high as 50,000× revealed a total loss of pore detail. Thin sections of untreated Celgard 2400 samples showed a similar loss of pore detail.

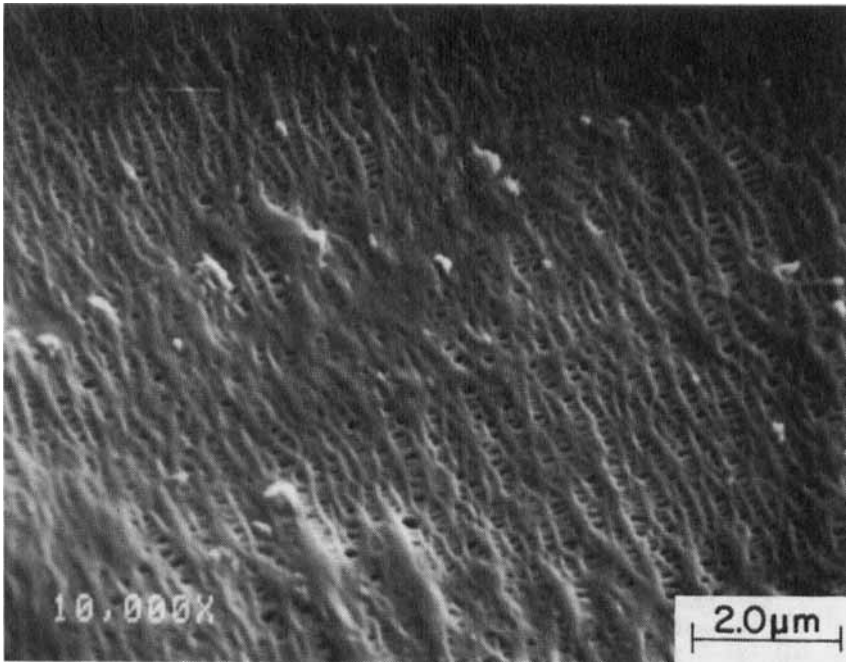

FIG. 1. Photomicrograph of untreated Celgard 2400 film, face view.

The widths of the thin sectioned films were measured to be about 27 μm. This width difference confirms the 1% film swelling reported previously for Celgard soaked in a 0.2 kmol/m^3 HDNNS–dodecane solution.

Pore Size Distribution of Celgard 2400

The pore size distribution of Celgard 2400 was determined after soaking several film samples in a 0.2 kmol/m^3 HDNNS–dodecane solution for 17, 27, and 41 d, respectively. The resulting pore size distributions are represented graphically in Fig. 15. The data were normalized on a gram sample basis.

DISCUSSION

In the photomicrographs of the untreated Celgard 2400 and 2500 samples, the surface pores appeared as a regular pattern of slots of fairly narrow size

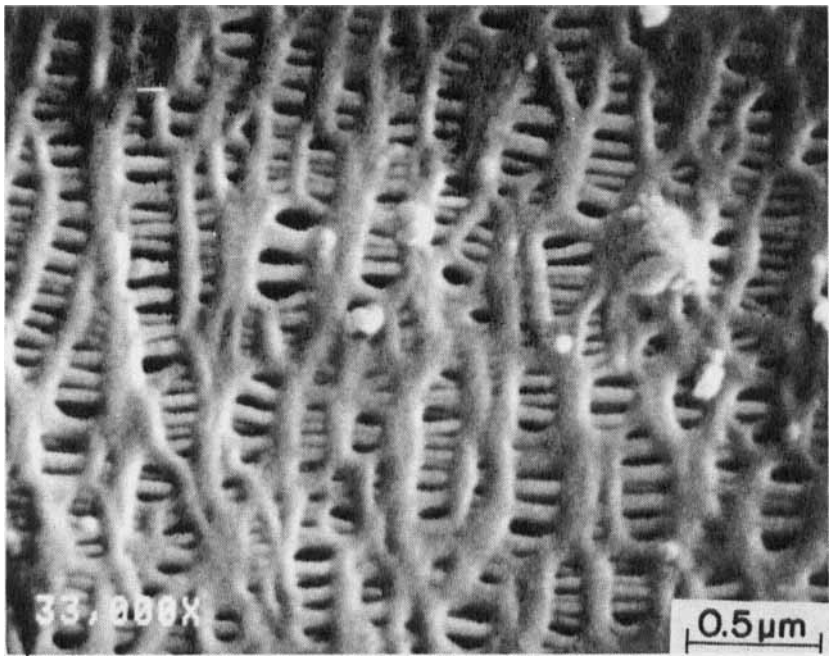

FIG. 2. Photomicrograph of untreated Celgard 2400, face view.

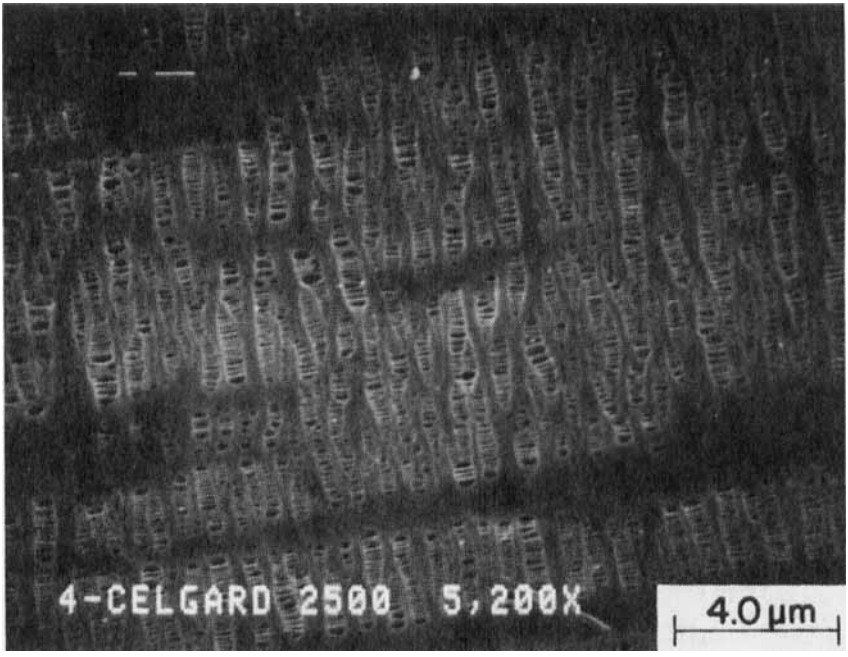

FIG. 3. Photomicrograph of untreated Celgard 2500, face view.

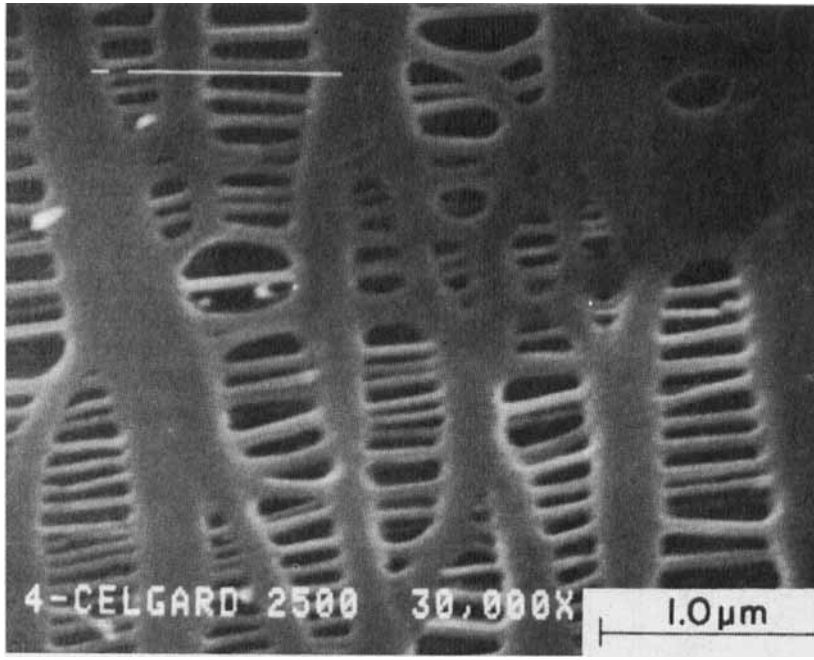

FIG. 4. Photomicrograph of untreated Celgard 2500, face view.

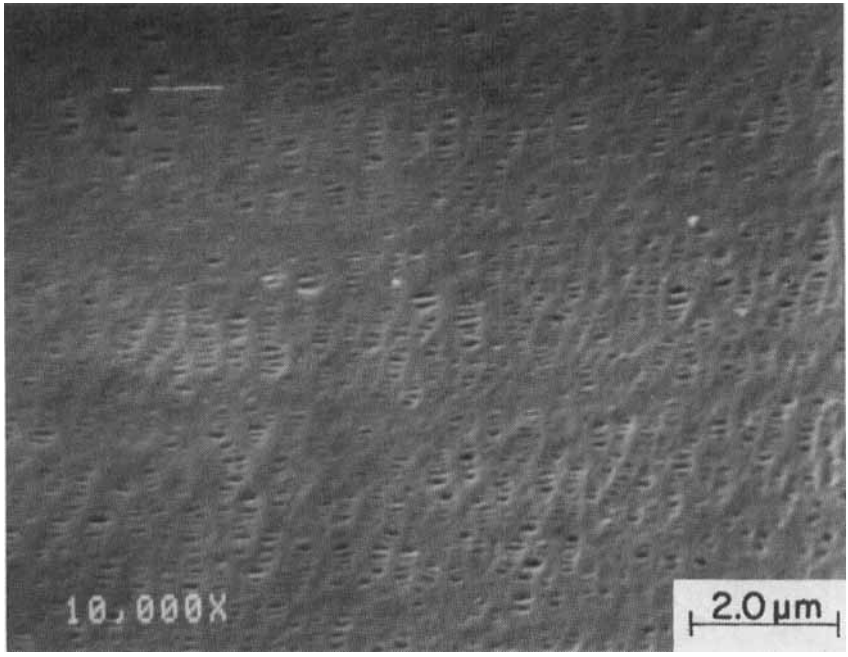

FIG. 5. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d, face view.

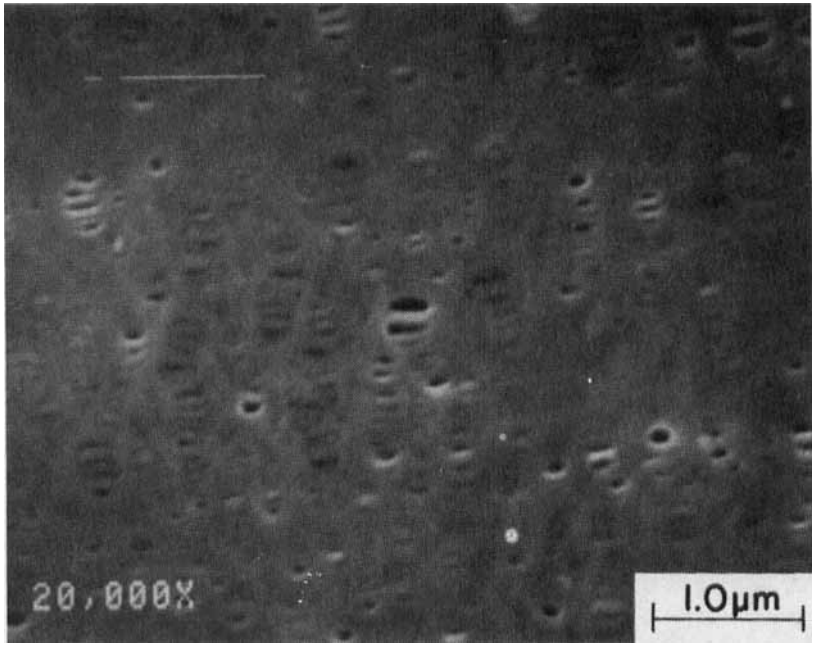

FIG. 6. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d, face view.

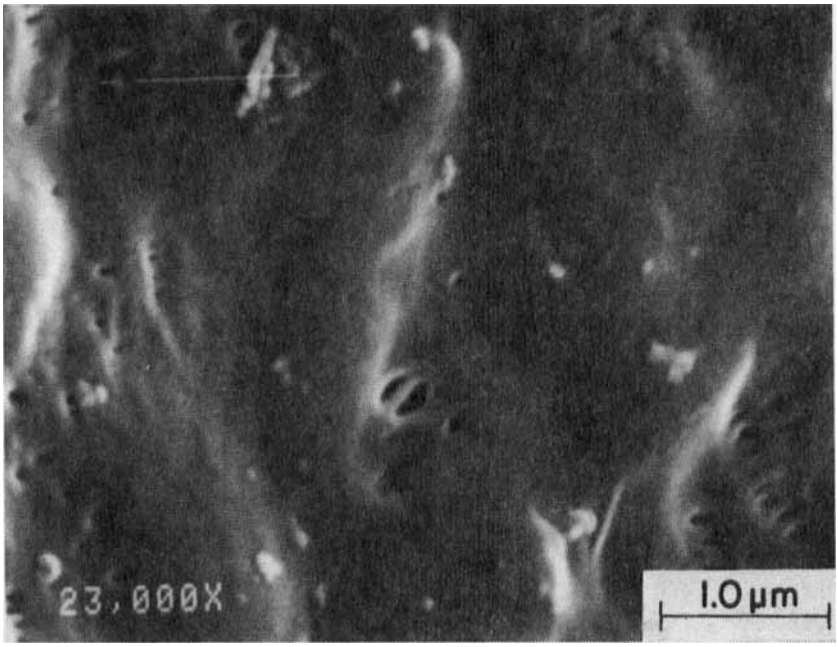

FIG. 7. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d, face view.

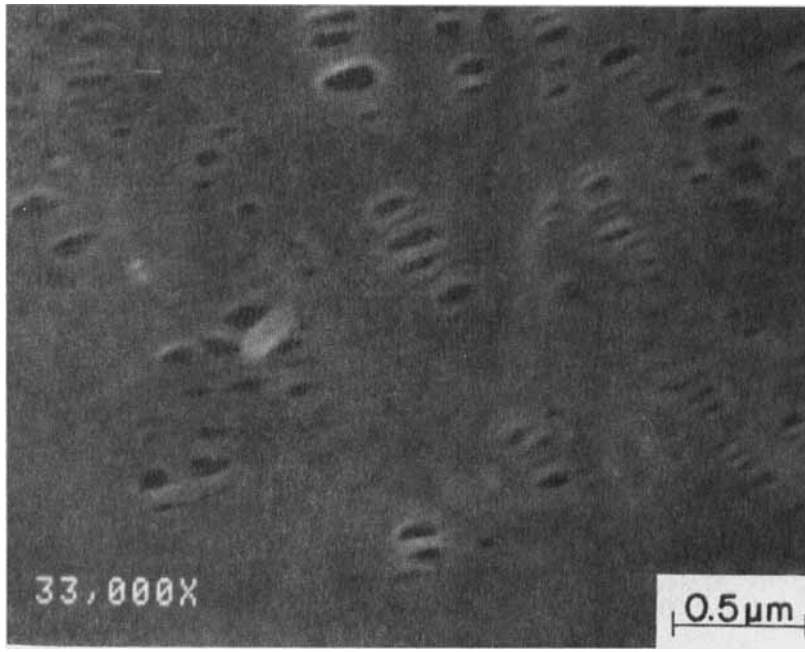

FIG. 8. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d, face view.

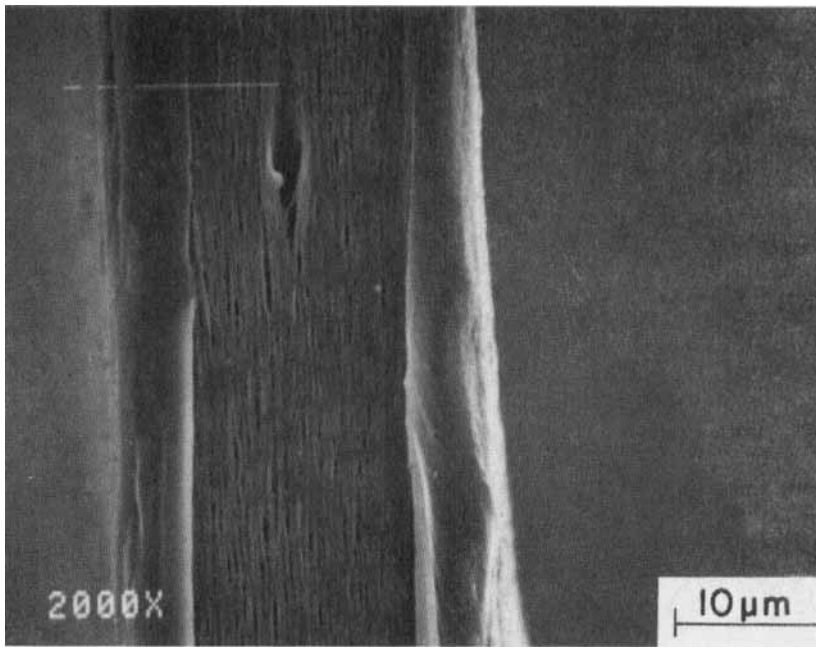

FIG. 9. Photomicrograph of untreated Celgard 2400, edge view.

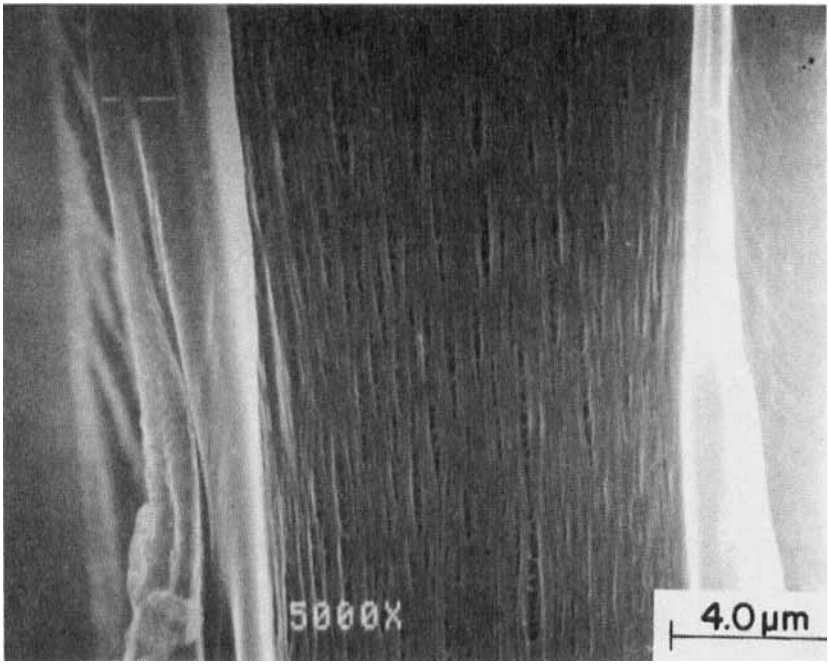

FIG. 10. Photomicrograph of untreated Celgard 2400, edge view.

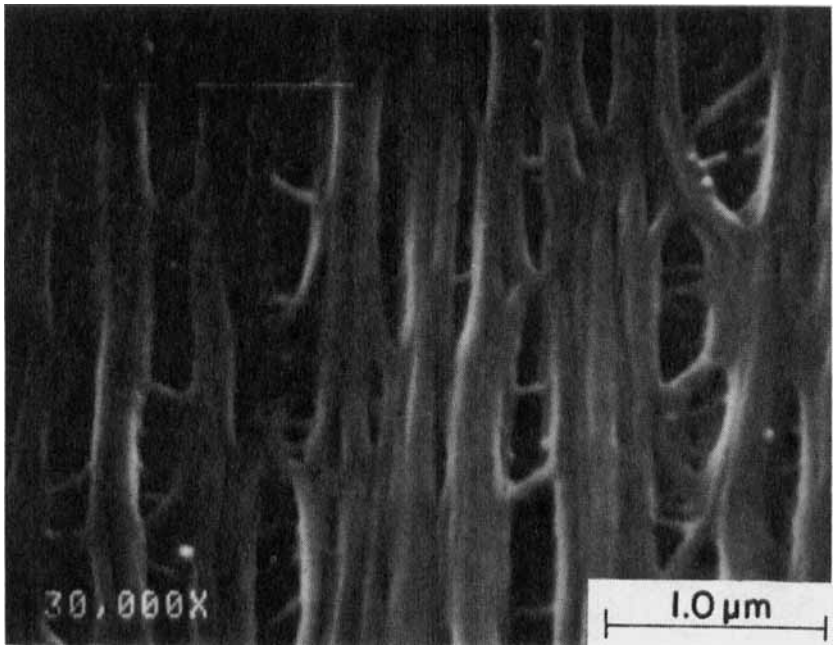

FIG. 11. Photomicrograph of untreated Celgard 2400, edge view.

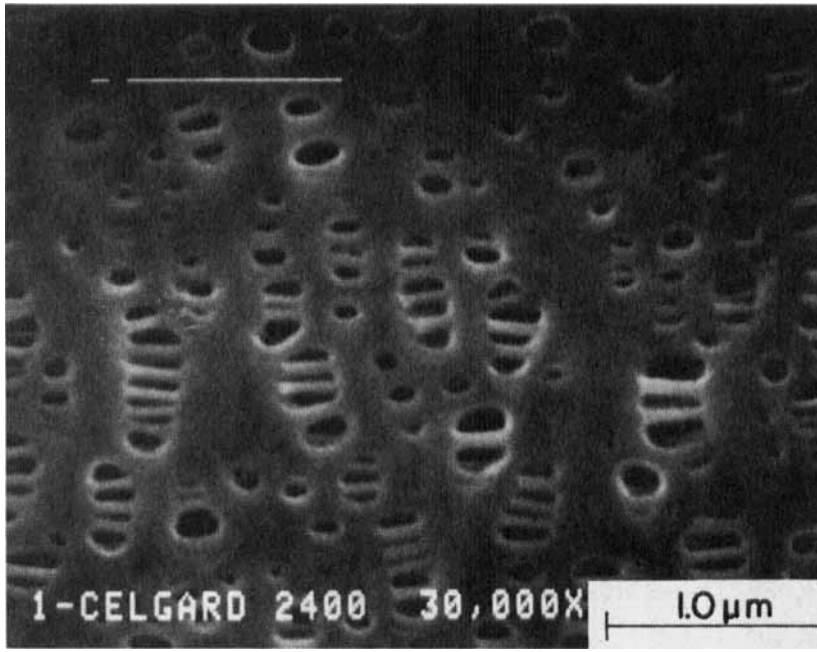

FIG. 12. Photomicrograph of untreated Celgard 2400, face view.

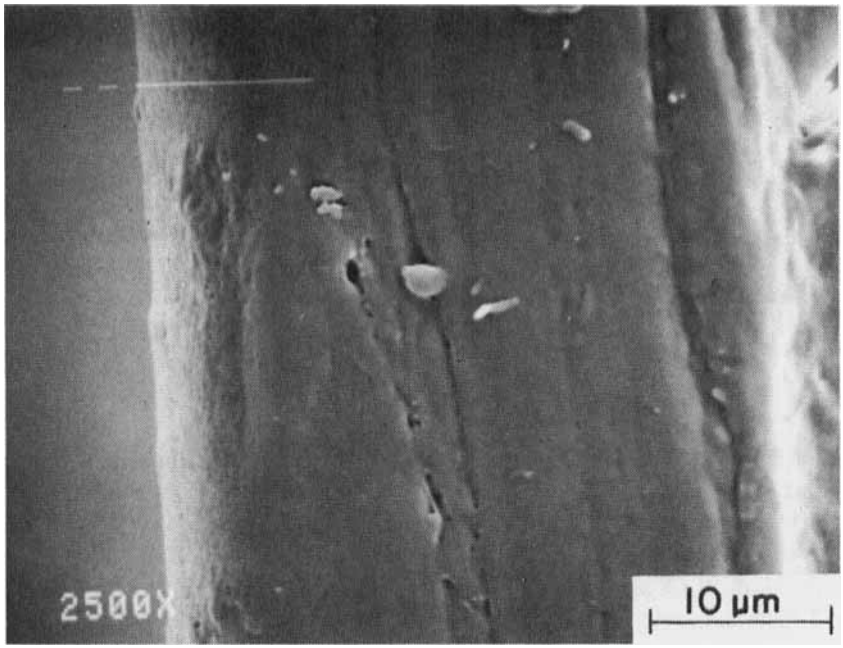

FIG. 13. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d, edge view.

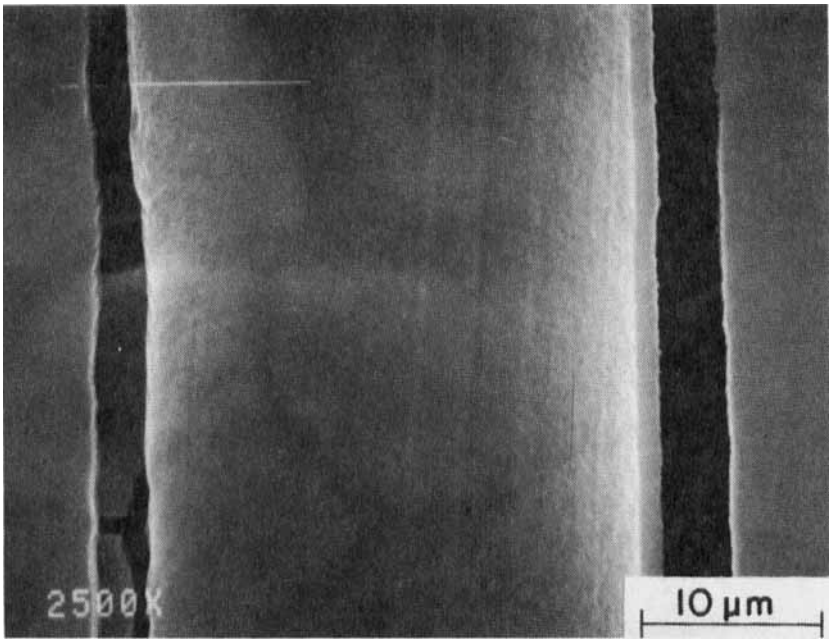

FIG. 14. Photomicrograph of Celgard 2400 impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d and prepared as a thin section.

distribution. The film edges of untreated Celgard 2400 measured approximately 25 µm in width. The measured film width agrees with the value published in the manufacturer's literature (*8*).

All cut film edges, whether soaked in an HDNNS–dodecane solution or not, showed an almost complete loss of pore structure as illustrated in Fig. 13. The apparent pore fusion was probably a result of high temperature and pressure generated during the cutting process.

Celgard 2400 was also examined for evidence of structural alteration after having been impregnated with a 0.2 kmol/m^3 HDNNS–dodecane solution for 55 d. Figures 6 and 7 are typical face images obtained from the treated film samples. The treated film samples showed an increase in both number and size of localized areas which contained no pores.

Thin sections of treated film samples were examined with two objectives: (a) to obtain a representative view of the membrane structure as it appears when impregnated with the organic extractant solution, and (b) to impregnate the film with an epoxy resin in order to support the film fibers, thus preventing structural changes which might otherwise occur when cutting the

film. However, all thin sectioning attempts failed to preserve any pore structure. The complete loss of pore detail is attributed to the thin sectioning process and not to any chemical reaction between the HDNNS–dodecane solution and the film. This interpretation is supported by the fact that thin sections of both treated and untreated samples showed a similar loss of pore detail.

The pore size distributions found in Fig. 15 indicate that the pores of Celgard 2400 are present as a very narrow size distribution: 0.01 μm < 90% < 0.062 μm, with a median pore radius of 0.034 μm. The manufacturer lists an average pore size of 0.02 μm obtained by transmission electron microscopy (*8*). The pore size distributions of the treated samples are practically identical at the upper end of the size scale; however, the treated samples show a steady decrease of pore volume corresponding to radii less than 0.01 μm. The sharp drop in the cumulative curves at approximately 0.003 μm is due to the fact that the mercury intrusion technique used was not sensitive to radii less than 0.0021 μm.

SUMMARY AND CONCLUSIONS

The results presented in this study indicate that membrane support degradation may occur under liquid membrane extraction conditions. The observed pore fusion could have a detrimental effect on extraction rates and would seriously limit the lifetime of the membrane support. The results of this study indicate that the working lifetime of a supported liquid membrane should be considered not only in terms of organic phase dissolution, but also in terms of the chemical reactivity between the organic phase constituents and the support material. The rate of membrane degradation observed in this study is such that several weeks are required before a noticeable change begins to occur in the internal pore size distribution obtained by mercury porosimetry. However, after 55 d surface changes are clearly visible in the electron micrographs of the treated film samples.

Continuous extraction studies are needed in order to quantitatively assess the rate and extent of membrane degradation in terms of the effects on membrane extraction rates. Knowledge about the nature of the interactions between the porous film support and the organic phase is also needed to help in the design of more resistant film materials.

Acknowledgments

Special thanks are due to Rosemary Walsh and Tom Doman for their generous help with the SEM work. This research was supported by the

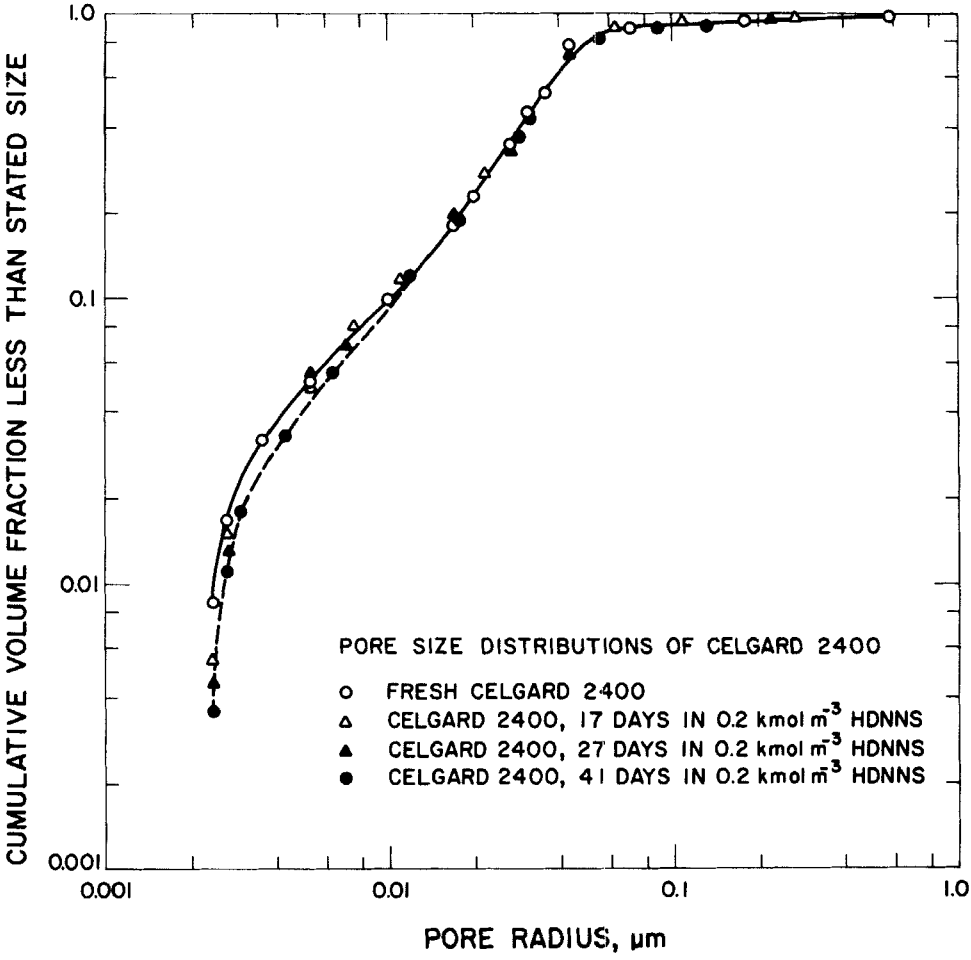

FIG. 15. Pore size distribution of a fresh Celgard 2400 sample and Celgard 2400 samples impregnated with a 0.2-kmol/m^3 HDNNS-dodecane solution for 17, 27, and 41d.

National Science Foundation under Grant No. CPE8110756. D.J.C. acknowledges fellowship support by the Mining and Mineral Resources Research Institute, The Pennsylvania State University.

REFERENCES

1. T. Largman and S. Sifniades, "Recovery of Copper (II) from Aqueous Solutions by Means of Supported Liquid Membranes," *Hydrometallurgy, 3,* 153–162 (1978).
2. D. J. Chaiko and K. Osseo-Asare, "Cobalt Extraction by HDNNS Liquid Membranes I: Characterization of the Extraction System," *J. Membr. Sci.,* Submitted.
3. D. J. Chaiko and K. Osseo-Asare, "Accelarated Coupled Transport (ACT): Cobalt Extraction by LIX63-HDNNS Liquid Membranes," *Metall. Trans., B,* Submitted.
4. K. Osseo-Asare and M. E. Keeney, "Aspects of the Interfacial Chemistry of Nickel Extraction with LIX63-HDNNS Mixtures," *Ibid., 11,* 63–67 (1980).
5. M. Ostler, Private Communication, Celanese Plastics Co., Summit, New Jersey, 1981.
6. A. W. Adamson, *Physical Chemistry of Surfaces,* 3rd ed., Wiley, New York, 1976, pp. 9–11.
7. S. Lowell, *Introduction to Powder Surface Area,* Wiley, New York, 1979, p. 92.
8. Anon., *Celgard Microporous Polypropylene Film, Technical Information,* Celanese Fibers Marketing Co., Charlotte, North Carolina, 1980.

Received by editor May 24, 1982