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HOLLOW FIBER MEMBRANES FOR PHOTOSENSITIZED ELECTRON TRANSPORT

Carl C. Wamser, John W. Otvos, and Melvin Calvin

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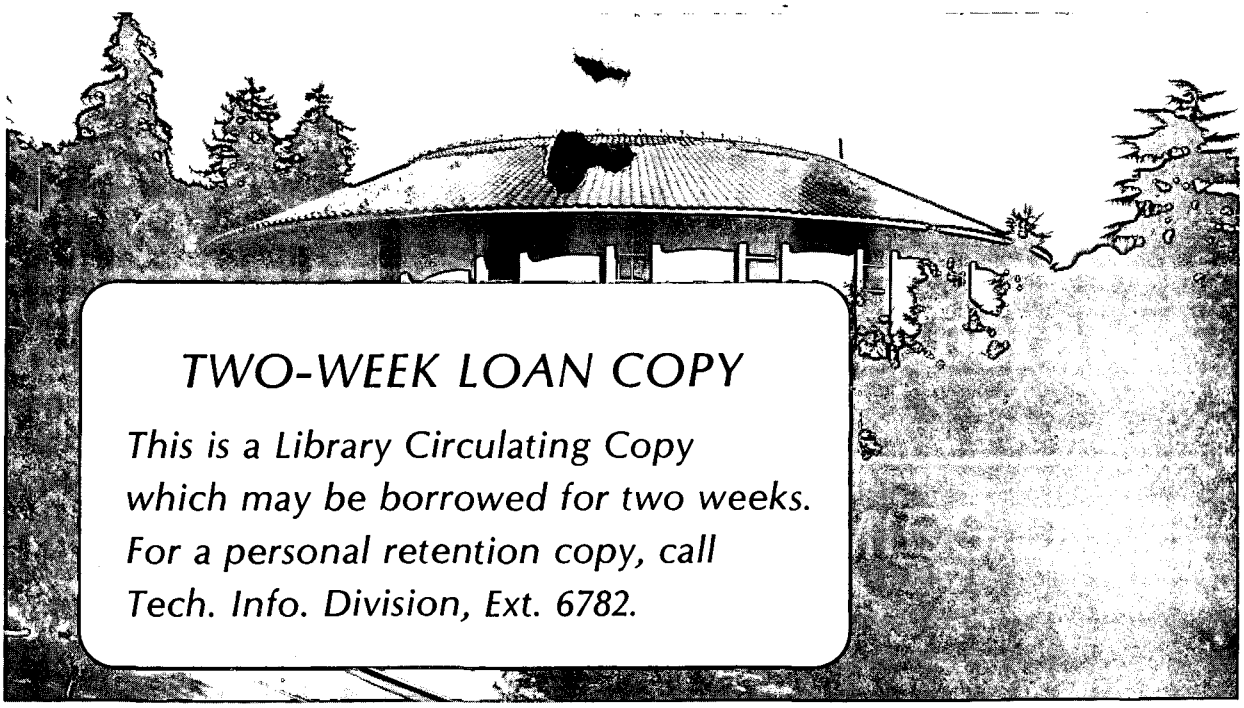

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HOLLOW FIBER MEMBRANES FOR PHOTOSENSITIZED ELECTRON TRANSPORT

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January 1981

Abstract: Commercially available cellulose acetate hollow fiber membranes have been investigated for possible use in artificial photosynthesis solar energy schemes. The function of the membrane is to contain the photosensitizer and to separate the oxidized and reduced species which result from photosensitized electron transfer reactions on each side of the membrane wall. Membranes were successfully modified by a process of soaking in a THF solution saturated with porphyrin, followed by a water rinse. This procedure gives dark purple fibers which contain up to 30 mM zinc tetraphenylporphyrin in the fiber walls. A "plumbing" system has been developed to allow flow of a solution through the inner channels of a 24-fiber bundle while it is immersed in a separate outer solution. Preliminary studies indicate that the fibers are somewhat permeable to both EDTA and dimethyl viologen, the electron donor and acceptor molecules, respectively. Preliminary photochemical studies on cut-up pieces of the treated fiber indicate that it does photosensitize a reaction between EDTA and dimethyl viologen in aqueous solution.

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Introduction: The term "artificial photosynthesis" is used to describe any solar energy conversion scheme which is designed to accomplish a photoinduced separation of an oxidant and a reductant across a phase boundary. In photosynthesis, the photosynthetic membrane provides the boundary across which oxidation and reduction capability is separated. In artificial photosynthesis, the phase boundary is most commonly provided by a micelle, a vesicle, or a membrane.

A separate, accompanying report describes in detail a generalized scheme for artificial photosynthesis and the kinetics expected for the mechanism presented. This report will describe experimental work aimed at development of hollow fiber membranes for use in artificial photosynthetic schemes.

The generalized reaction scheme (Figure 1) utilizes a membrane to separate the oxidized electron donor (D^+) from the reduced electron acceptor (A^-). Thus the photosensitizer (S) must be located in the membrane and capable of interaction with both the donor and acceptor. One of the primary requirements is the necessity of transporting the oxidized sensitizer (S^+) from one side of the membrane (where it has reduced A to A^-) to the other side of the membrane (where it can oxidize D to D^+). This is most readily accomplished by a simple electron transport across the membrane. This step is likely to be the limiting factor in the efficiency of such a system (described in more detail in the accompanying report on kinetics).

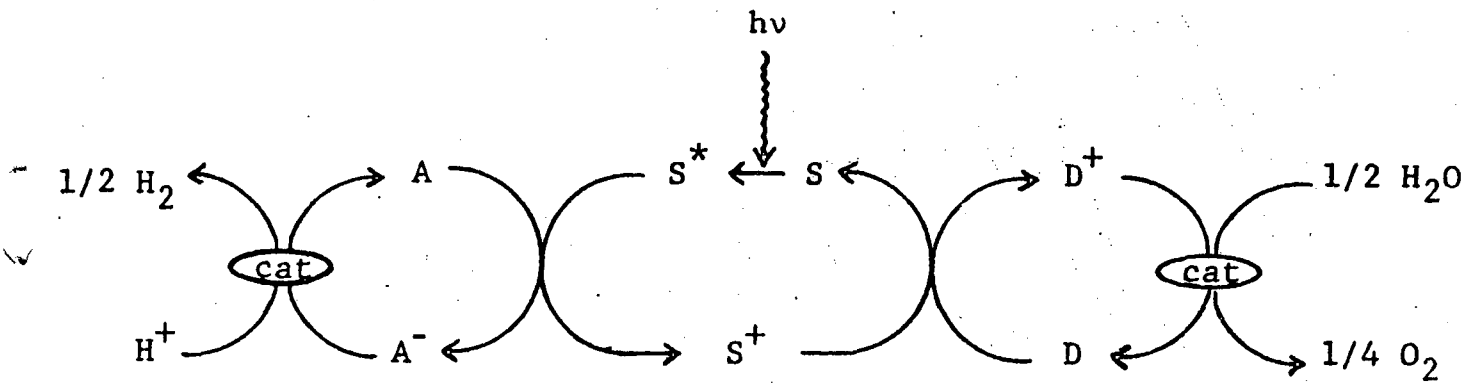
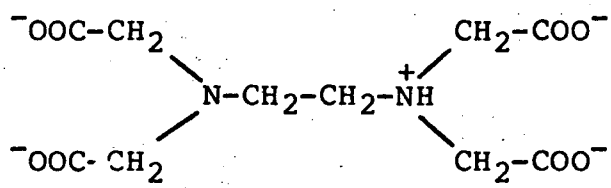
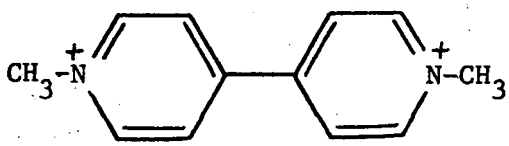


Figure 1 - Cyclic photochemical scheme for decomposition of water



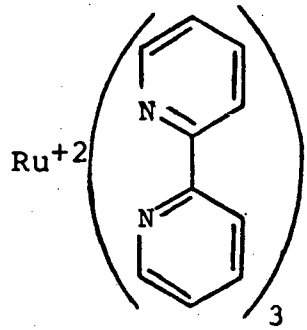
Ethylenediaminetetraacetic acid (EDTA)

(in -3 ionized state, 6<pH<10)

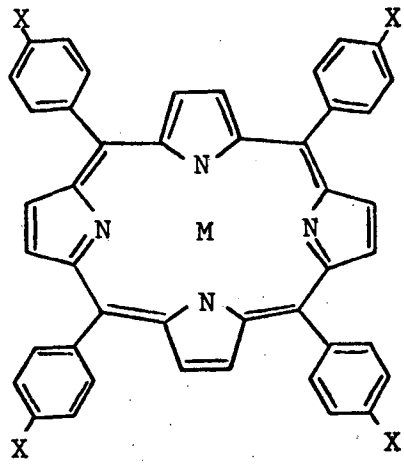


Dimethyl viologen (MV^{+2})

Figure 2 - Electron donor and acceptor molecules



Ruthenium(II)tris-bipyridyl ($Ru(bipy)_3^{+2}$)



Tetraphenyl porphyrin
TPP (M = 2 H, X = H)

Tetra(4-carboxyphenyl) porphyrin:
TCPP (M = 2 H, X = -COOH)

Tetra(4-sulfonatophenyl)-porphyrin:
TSPP (M = 2 H, X = $-SO_3^-$)

Metalloporphyrins:
e.g.,ZnTPP (M = Zn, X = H)

Figure 3 - Photosensitizers

Figures 2 and 3 illustrate the molecules commonly used in artificial photosynthetic schemes. One successful artificial photosynthetic scheme is that developed by Ford (W.E. Ford, Ph.D. Thesis) utilizes a vesicle to provide a phase boundary: a phospholipid bilayer membrane which contains an interior aqueous solution with EDTA as electron donor. The exterior aqueous solution contains methyl viologen (MV^{+2}) as electron

acceptor. The sensitizer is $Ru(bipy)_3^{+2}$, modified to have long alkyl chains to keep it attached to the lipid bilayer membranes. Since the Ru^{+2} "head" of the sensitizer is hydrophilic, this tends to protrude into the aqueous solutions (both interior and exterior) while anchored to the membrane by it nonpolar "tails". These vesicles have the advantage of a very thin membrane (about 4 nm), and the mechanism of electron transport is considered to be electron tunneling from an interior Ru^{+2} to an exterior Ru^{+3}.

The primary disadvantage of a vesicle for a solar energy conversion scheme is the size limitation on the internal contents. As the electron donor is gradually exhausted from the interior solution, the reaction must slow down and eventually stop. For a continuously operational system, flow systems would be desirable, allowing a continuous feed of donor (and removal of D^+) and a continuous feed of acceptor (and removal of A^-). The simplest modification would extend the spherical shape of the vesicle to a cylinder, with an interior channel available for the donor solution, and the acceptor contained in the exterior solution. Cylindrical membranes are commercially available, called hollow fiber membranes. This report describes modifications of cellulose acetate hollow fiber membranes and a preliminary evaluation of their applicability as artificial photosynthesis membranes.

Properties of Hollow Fiber Membranes:

A length of cellulose acetate hollow fiber membranes (24 fibers per bundle) was obtained from Dow Chemical (Walnut Creek). The data sheet for the fibers is attached as Appendix 1, and the most relevant properties are summarized in the following section. Typical dimensions of a hollow fiber membrane are illustrated in Figure 4.

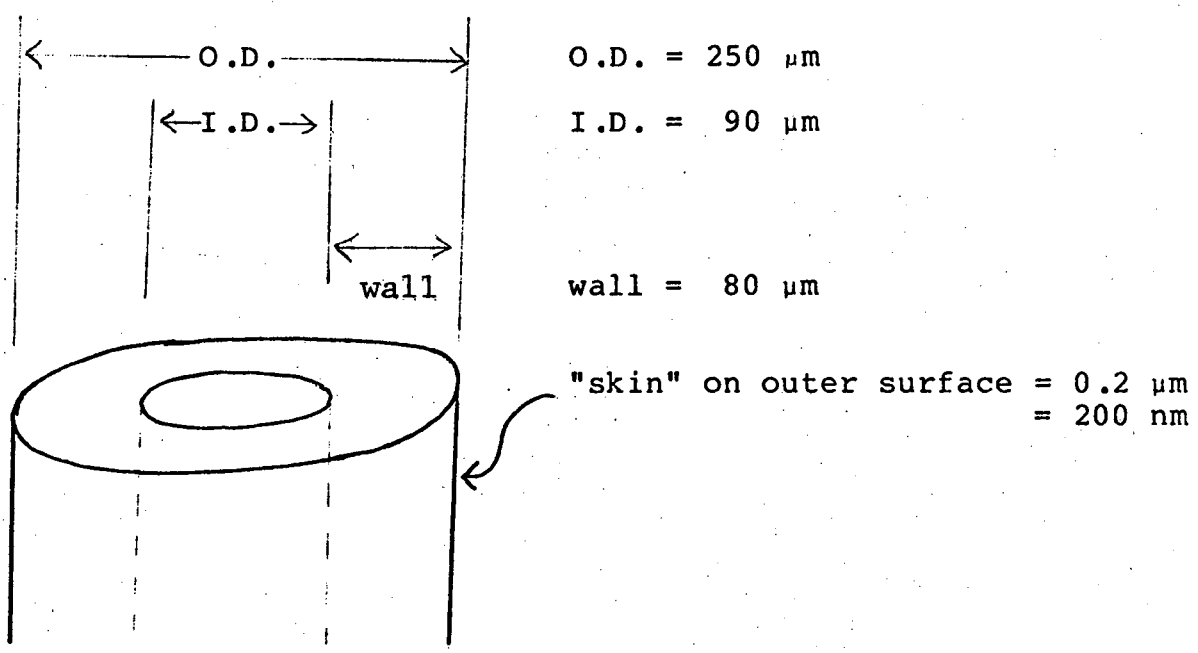


Figure 4 - Hollow Fiber Membrane (Dow)

Under a microscope at about 50x magnification, the inner channel is clearly visible, about equal in diameter to the wall thickness. The walls themselves are designed to be extremely porous, essentially serving as a structural support for an outer "skin" which is only 0.2 μm thick, but which serves as the functional membrane. This "skin" limits the

permeability of the overall fiber (between the inner and outer solutions). Thus depending upon the specific treatment of the fiber, it may serve as a dialysis membrane (allowing only small molecules to permeate from the inner to outer solutions), or with a reduced permeability it may serve as a desalination membrane (allowing water to permeate through but not salts). Permeability is controlled by an annealing process: heating the fibers irreversibly reduces their permeability. Typical fibers as obtained from Dow were unannealed, and Tom Davis (Dow Chemical, Walnut Creek) estimated that they would be permeable to molecules of molecular weight under 100 only.

The chemical composition of the fibers is linear, non-crosslinked polymers of cellulose triacetate, average M.W. about 88,000 (viscosity weight-average), with just a few of the cellulose hydroxyl groups non-acetylated (calculated one in 12 glucose units has a free hydroxyl). The fibers are extensively hydrogen-bonded to water and must be kept wet. Allowing to air dry or even heating in water leads to loss of this incorporated water and an irreversible decrease in permeability. Thus the fibers are always stored under water and are rinsed with fresh distilled water occasionally.

Solvents were found to interact with the fibers in one of three ways: (1) Insoluble - in many solvents, the fibers remain strong and keep their shape well; solvents of this type include water, alcohols, hydrocarbons, carbon tetrachloride, and ethyl ether. (2) Soluble - some highly polar organic solvents completely dissolve the fibers, such as dioxane, sulfolane,

dimethyl sulfoxide, N-methylpyrrolidone, chloroform, and dichloromethane. (3) Swelling - some solvents apparently penetrate and swell the fibers but do not dissolve them. In these solvents the fibers are soft and fragile but generally maintain the integrity of their cylindrical shape. These solvents include tetrahydrofuran (THF), acetone, butanone, ethyl acetate and glyme.

Porphyrin Incorporation into Hollow Fiber Membranes:

Initial plans considered covalent attachment of functionalized porphyrins to the cellulose acetate membranes, perhaps through available free hydroxyl groups. While this method has the advantage of a stable attachment, it has the disadvantage of a relatively difficult synthetic sequence: an appropriate functionalized porphyrin must be synthesized and then attached at relatively unreactive sites (free hydroxyls which did not react with acetic anhydride in the original acetylation of cellulose). Furthermore, the attachment may be primarily at the surface, rather than throughout the membrane, which would be required for efficient electron transport.

A much simpler method was developed based upon a soaking procedure. A typical procedure is described in detail. A convenient length of a hollow fiber bundle (about 20 cm of a 24-fiber bundle) is cut off and placed (still damp with water) inside a 6 mm glass tubing of somewhat greater length (e.g., 30 cm). One end of the tubing is tightly corked and the tubing is filled with a saturated solution of ZnTPP in THF. Frequently excess crystals of undissolved ZnTPP are also included to assure a saturated solution. A small air bubble is left in the tubing to assist in mixing and visibility, and the other end is tightly corked. The fibers should be extended their full length. The fibers tend to stick together, but this can be minimized by a gentle rolling and tilting of the tubing; this also allows one to see the fibers and to stir the solution occasionally.

After soaking overnight, the soaking solution is drained carefully. While in THF, the fibers are extremely fragile, so they should be kept inside the tubing until the following water rinse has been completed. The best procedure is to tilt the tubing at a gentle angle, remove one cork from the top of the tubing, then loosen the bottom cork to allow the solution to drain slowly while holding the fibers within the tubing. Immediately the tubing is filled with water and this is also drained. This time the fibers can be removed as the water drains. Rinse the fibers thoroughly under running water, carefully separating any fibers that might be stuck together. Trim the ends to make them even and to make fresh openings, and store under water until ready to use. The fibers are dark red-purple, essentially the color of the starting ZnTPP. Upon standing in water a few days, the fibers take on a much darker purple color.

Similar treatments have been performed with TPP in THF and with ZnTPP in acetone. The acetone treatment gave fibers of somewhat more uniform appearance under the microscope, but lesser ZnTPP content. Including an intermediate step of rinsing with fresh THF before the water addition was found to give substantially lower ZnTPP content; this step was generally omitted.

Microscopic Appearance of Treated Hollow Fibers:

Microscopic photographs of typical samples of treated hollow fibers are shown in Appendix 2. Many more photos are also available as slides - C.C. Wamser notebook references: pages 27, 39, 73. The standard procedure gives dark purple fibers of the same approximate size and cylindrical shape as before treatment (see Appendix 2, photos 1 and 3). The inner channel is frequently twisted and contorted, however; visibility of the inner channel is greatly enhanced if an air bubble is trapped in the inner channel. Crystals are found on the surfaces of the fiber, apparently located on both the inner and outer walls (photo 4).

Inclusion of a THF rinse in the treatment gives fibers much lighter in color but more uniform (most crystals are gone) (photo 6). Use of acetone as the soaking solvent gives fibers which have retained their cylindrical integrity very well (photo 7). Annealing the fibers by heating in boiling water seems to dissolve the crystals into the cellulose acetate; the fibers retain their deep purple color but no crystals are evident; the shape of the fiber is substantially more contorted, however (photo 5).

Calculations of Porphyrin Content:

A quantitative determination of the amount of ZnTPP incorporated into the fibers was obtained by dissolving a known length of the treated fibers in a standard volume of dioxane, and analyzing the UV-visible spectrum for ZnTPP (using ε(552 nm) = 22,000; ε(589 nm) = 7000). A typical analysis would involve a 3 cm length of a bundle of 24 fibers dissolved in 10 ml of dioxane. Using the fiber dimensions cited earlier, the volume of the fiber wall is calculated to be 0.43 μl per cm length of one fiber (for comparison, the internal volume is 0.064 μl per cm length of one fiber). The calculated number of moles of ZnTPP per fiber wall volume gives an effective concentration of ZnTPP in the membrane. Typical values are listed below:

Treatment	ZnTPP Content
TPP (THF)	20 mM
TPP (THF) with rinse	2 mM
ZnTPP (THF)	32, 28 mM
ZnTPP (THF) with rinse	5 mM
ZnTPP (acetone)	11, 8 mM

Hollow Fiber "Plumbing" System:

To provide a flow system for the inner channels of the fibers, each end of a 20 cm length of a 24-fiber bundle is epoxied into a length of 12 gauge teflon tubing. (Later experiments have used tygon tubing, which provides a much better seal to epoxy.) The ends of the fibers must be inserted far enough up the tubing to assure that they are not clogged by epoxy. This connection is then epoxied into a small piece of 6 mm glass tubing, to provide an additional seal and to allow insertion into a thermometer adapter. The fibers are kept damp with water at all times during this procedure. A diagram of the resultant connection is shown in Figure 5.

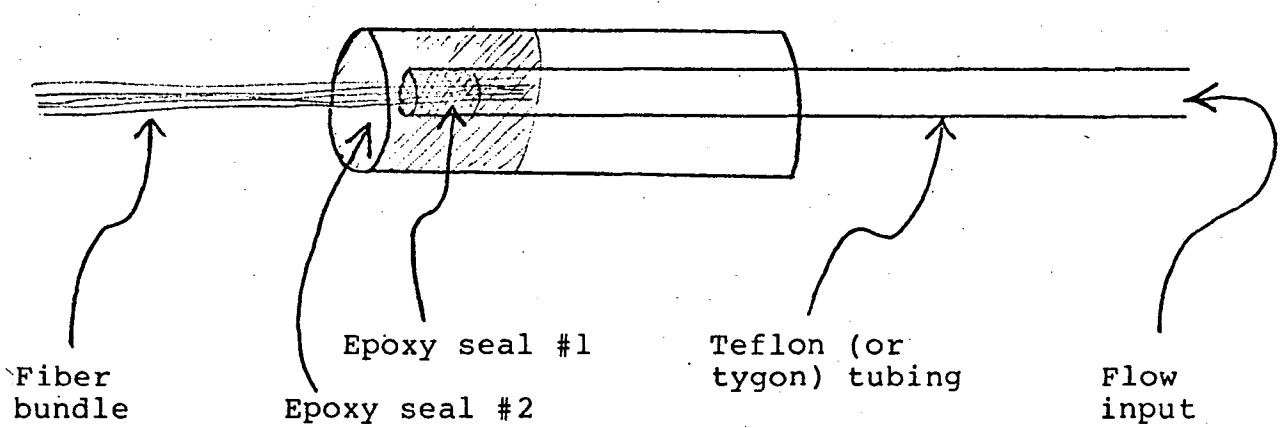


Figure 5 - Connector for Hollow Fiber Flow System

Once the epoxy sets, the fiber bundle is immersed in a flask containing the exterior solution. A peristaltic pump provides the pressure to force the interior solution through the inner channels. At the end of the system, a flow monitor can be located. Figure 6 shows a schematic of a typical flow system.

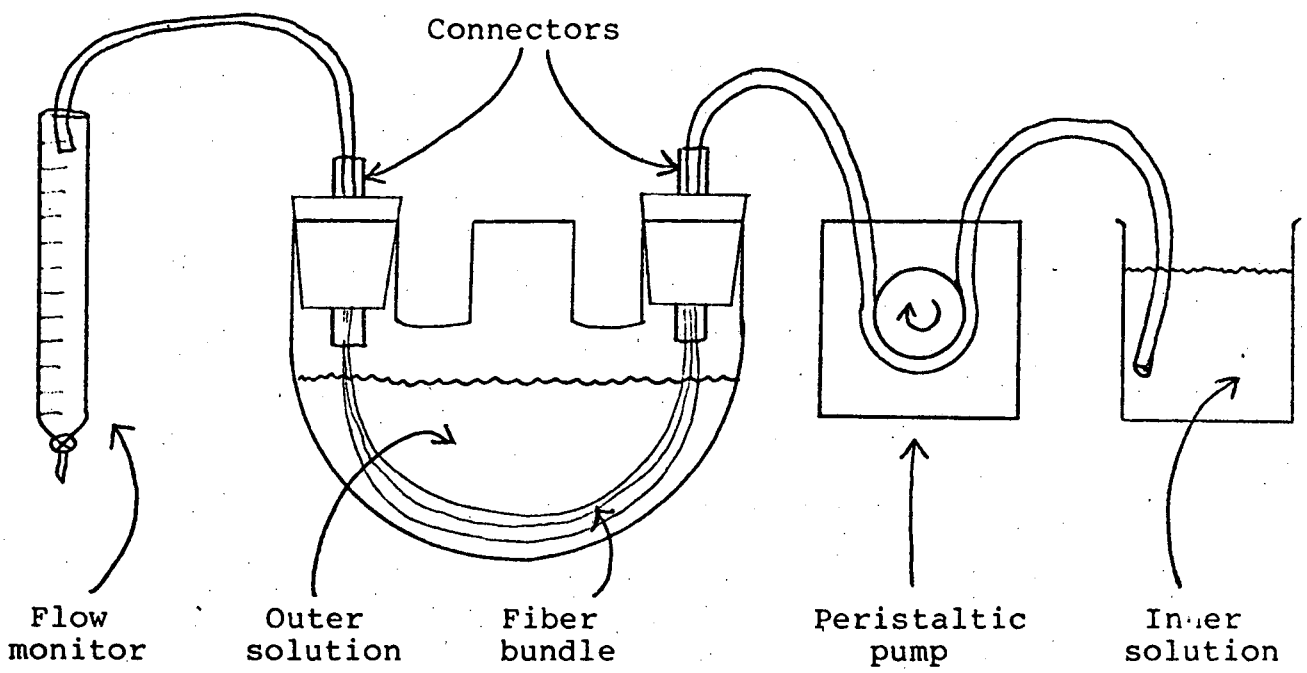


Figure 6 - Hollow Fiber Flow System

Because of their small inside diameter, the fibers provide a high resistance to flow. This resistance is even greater after the treatment to incorporate porphyrin, apparently because the inner channel appears to be more contorted. The peristaltic pump originally used (LKB Bromma 12000 Varioperpex) was capable of providing sufficient pressure for a good flow through a bundle of untreated fibers, up to 2 ml per minute. If the fibers were annealed by heating to 70°,

the maximum flow rate attainable was 1 ml/min. However, since the interior volume of the fibers is so small (0.064 µl per cm of one fiber or 31 µl for a 20 cm length of a 24-fiber bundle), a rate of 1 ml/min will provide a rapid turnover of the interior solution (31 µl will flow through every 2 seconds). The peristaltic pump was incapable of pumping through the fibers treated with ZnTPP (THF), apparently because the pump could not develop sufficient pressure. Fibers treated with ZnTPP (acetone) could be pumped through, but they were easily broken during pumping, as evidenced by air leakage. The fragility of these fibers may be due to their thinner walls, as seen in microscope photographs, since acetone is reported to be capable of dissolving cellulose acetate slightly.

Later experiments at Cal State Fullerton used a linear (not rotary) peristaltic pump (Harvard Apparatus) which delivered sufficient pressure to pump through fibers treated with ZnTPP (THF), at a flow rate intentionally kept low, about 0.1 ml/min.

Hollow Fiber Permeability Studies:

The hollow fiber membranes are designed to separate the donor and acceptor solutions; therefore, they should be impermeable to the molecules used as donor and acceptor, EDTA and MV^{+2}, respectively. The actual flow apparatus will operate with the donor in the inner channels and the acceptor in the exterior solution. There are at least two reasons that this would be the more favorable arrangement: (1) the actual photochemical reaction is between the sensitizer and acceptor, and this should take place on the outer surface where more light is absorbed; (2) the reduced acceptor undergoes ready back-reaction with oxidized sensitizer, so it should not be confined to a small volume such as the inner channel or reaction efficiency would drop off steadily along the flow channel. It can be calculated that the inner channel can contain sufficient EDTA to reduce a significant amount of MV^{+2} (31 µl of 0.1M EDTA contains 3 µmoles, which could convert 6 µmoles of MV^{+2} to MV^{+}, which would give an O.D. > 2 at 602 nm in 20 ml of solution). Furthermore, EDTA decomposes after serving as an electron donor, but its decomposition products are not harmful to the reaction efficiency.

Although the flow system will operate with EDTA in the inner channels, the permeability of the fibers to MV^{+2} was also tested, primarily because its UV absorption makes a simple and sensitive test. Since a flow system through treated fibers was never established at Berkeley, permeability studies were performed only on untreated fibers. A solution

of 0.06 M MV^{+2} in pH 7 buffer was circulated through the inner channels of an untreated fiber bundle, which were immersed in pH 7 buffer. After only 1 minute of pumping, the UV absorption of MV^{+2} was observed in the exterior solution (O.D. = 0.21 at 256 nm, corresponding to 10^{-5} M). After 5 minutes, the absorption had increased approximately proportionally (O.D. = 1.25). To ascertain that there was not a leak in the fibers, a deep blue dye solution was prepared from Blue Dextran (M.W. about 10^6) and recirculated through the inner channels for 30 minutes, allowed to stand overnight and pumped another 10 minutes (total volume recirculated was equivalent to about 100 ml). There was no trace of blue by eye or any visible absorption by spectrophotometry in the outer solution Thus the fibers did not have a gross leak, and the appearance of MV^{+2} was apparently by permeation through the fiber membrane.

The fibers were annealed by heating to 70° for 5 minutes. The permeability to MV^{+2} was tested under conditions identical to those described above. The permeability was somewhat reduced, but was still unacceptably high (O.D. = 0.22 (4 min), 1.08 (10 min), 1.83 (15 min)).

Permeability to EDTA was done on the same fibers, using a test devised by Ford (Ph.D. thesis). An indicator of nitroso-R salt and cupric chloride was prepared and used to detect the presence of EDTA by monitoring the visible absorption spectrum. A solution of 0.1 M Na_2 EDTA in pH 7 buffer (final pH 5.7) was pumped through the inner channels while the fibers were immersed in pH 7 buffer as the outer solution. Only a

single run was performed and there was no EDTA detected in the outer solution after 20 minutes of pumping (total volume pumped was about 50 ml). After 3 hours, EDTA was detected. The test is not easily quantitated, so the results were taken as simply positive or negative for permeation. It was demonstrated that the test is sensitive enough to detect 10^{-7} moles of EDTA. Thus the permeability to EDTA seems to be acceptably low, but these results require confirming experiments. The higher permeability to MV^{+2} may be less of a problem than it appears, since in the actual flow system visualized any permeation of MV^{+2} would occur from outside to inside and would be operating against a pressure gradient. Additional experiments will be performed to determine the rate at which MV^{+2} permeates from outside to inside the fibers, which is expected to be lower than the rate of permeation from inside to outside.

Photochemical Studies:

The ultimate purpose of the fibers is to accomplish specific photochemistry. However, until a flow system is established with treated fibers, the definitive photochemical experiments cannot be run. Some photochemical experiments were performed using treated fibers cut into small pieces, which served as a heterogeneous sensitizer for the reduction of MV^{+2} by EDTA. Rates were compared with the reaction sensitized by homogeneous ZnTSPP (water-soluble zinc tetra-sulfonatotetraphenylporphyrin). Conditons were held as constant as possible in the two cases: identical concentrations of 0.03 M MV^{+2}, 0.05 M EDTA and pH 8.65 were assured by using the same premixed solution; the same interference filter was used for irradiation (labelled 4300 Å but actual cutoffs were 412 and 429 nm (O.D. = 1) with maximum transmission at 422 nm); the cells were deoxygenated identically with three cycles of evacuation and argon purging; the same cell was used for both runs and was positioned in the same spot in front of the photolysis lamp (Oriel C-60-50 1000 watt xenon lamp). Two major problems led to an unreliability in the results, however. It was difficult to ascertain the relative amount of light absorbed in each case. The homogeneous sample was adjusted so essentially all of the incident light was absorbed (O.D.>2 at λ_{max} = 426 nm). In order to have all of the incident light absorbed by the heterogeneous sample, the cut-up pieces (each about 7 mm long) were piled in the bottom of the cell sufficient to block the light path.

Magnetic stirring helped to raise and agitate the pile of fibers. With stirring off, monitoring of reduced MV^{+2} could be performed in the homogeneous solution above the pile of fibers. Thus there is an assumption that all incident light was absorbed in each case. The second, more substantial problem, was that the sample of MV^{+2} used showed a long absorption tail into the visible (to about 500 nm), especially noticeable with the high concentrations (0.03 M) used in these experiments. A blank run with no added sensitizer gave a substantial rate of MV^{+} production.

Sensitizer	Rel. Rate
None	0.68
ZnTSPP	1.00
ZnTPP-fibers	0.33

The photochemical rate is apparently even slower with the treated fibers present than it would be with no sensitizer at all. These results are unsettling and require confirmation. Cleaner samples of MV^{+2} will be prepared (white rather than yellow crystals) to minimize the direct photolysis of MV^{+2}.

Further Work:

This work is being actively continued at California State University, Fullerton. Permission has been requested from the Department of Energy to allow inclusion of this work under a current research grant at CSUF which has Carl Wamser and John Olmsted as principal investigators. The primary focus will be to develop a functional flow system using fibers containing ZnTPP, and to determine the permeability parameters and then photochemical properties.

Acknowledgement: This work was performed during the fall semester of 1980 while Carl C. Wamser was on sabbatical from California State University, Fullerton. This work was supported, in part, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Appendix 1

Specifications and data on cellulose acetate hollow fiber membranes prepared and provided by Tom Davis, Dow Chemical Walnut Creek, Californa.

DOW CHEMICAL U.S.A.

September 10, 1980

RESEARCH CENTER
2800 MITCHELL DRIVE
WALNUT CREEK, CALIFORNIA 94598

415 · 944-2000

Carl Wamser
Melvin Calvin

NOTES ON CELLULOSE TRIACETATE FIBERS AND BEAKER UNITS

Each beaker unit contains 24 cellulose triacetate hollow fibers

Nominal dimensions are 90μ inside diameter, 250μ outside diameter

70°C annealed fiber has a high H_2O permeability; low NaCl permeablity

Unannealed fiber has a high H_2O and NaCl permeability, but should have a low permeability to species with $>10^2$ molecular weight; this has not been tested.

Permeability to species in ionized form will be much lower than to the unionized form.

Operating pH range is 2 to 8; outside this range the hydrolysis of the acetate groups increases rapidly.

Membrane is an asymmetric type; that is, outer surface of each fiber is a dense selective area which grades radially inward into a porous support structure.

Design operating pressure differential for external pressure minus lumen pressure is 400 psi.

Drying the fibers will irreversibly reduce their water permeability by $>10^3$.

Average acetyl content is 43.6%; the completely acetylated cellulose contains 44.8% acetyl; this is calculated as

$$100 \frac{\text{no. } CH_3CO \text{ per ring} \cdot \text{mol. wt. } CH_3CO}{\text{mol. wt. of triacetylated glucose ring}} =$$

$$100 \frac{43\ n}{288}$$

On the average 2.92 out of 3 glucose ring hydroxyls have been acetylated or there is about 1 hydroxyl for every 12 glucose units in the polymer chain.

The viscosity average molecular weight is about $88 \cdot 10^3$ or the viscosity average number of glucose units per chain is 309.

For additional information,

Tom Davis
944-2190

gs

Appendix 2

Color prints of representative microscope photographs of hollow fiber membranes - taken with a Zeiss camera and microscope available in LCB (Dr. Bartholomew's lab).

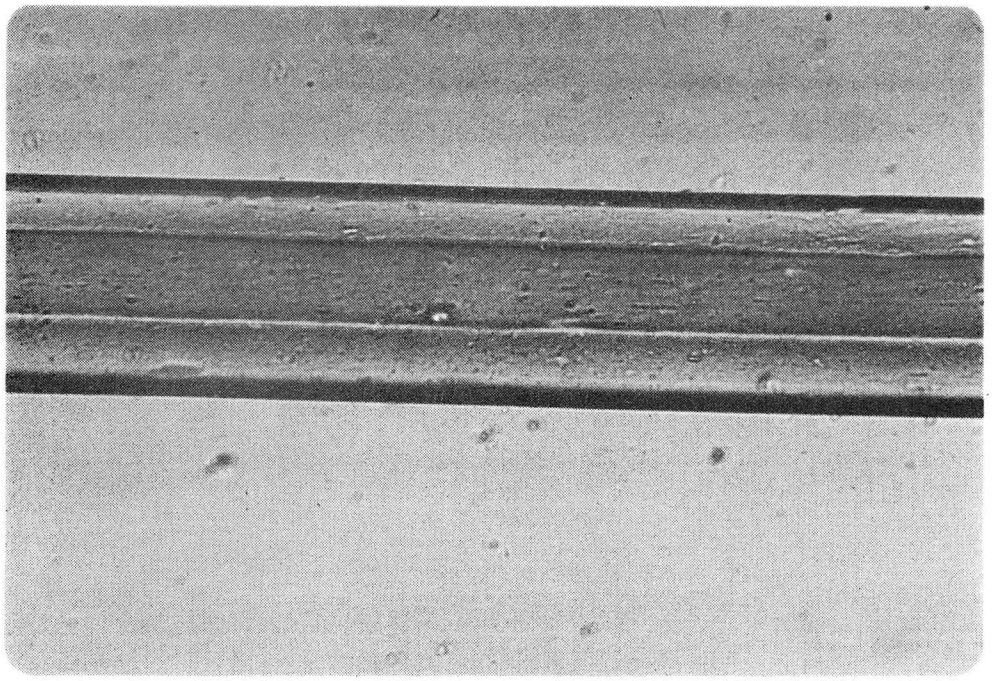


Photo 1 - Untreated cellulose acetate hollow fiber in water - (50x magnification)

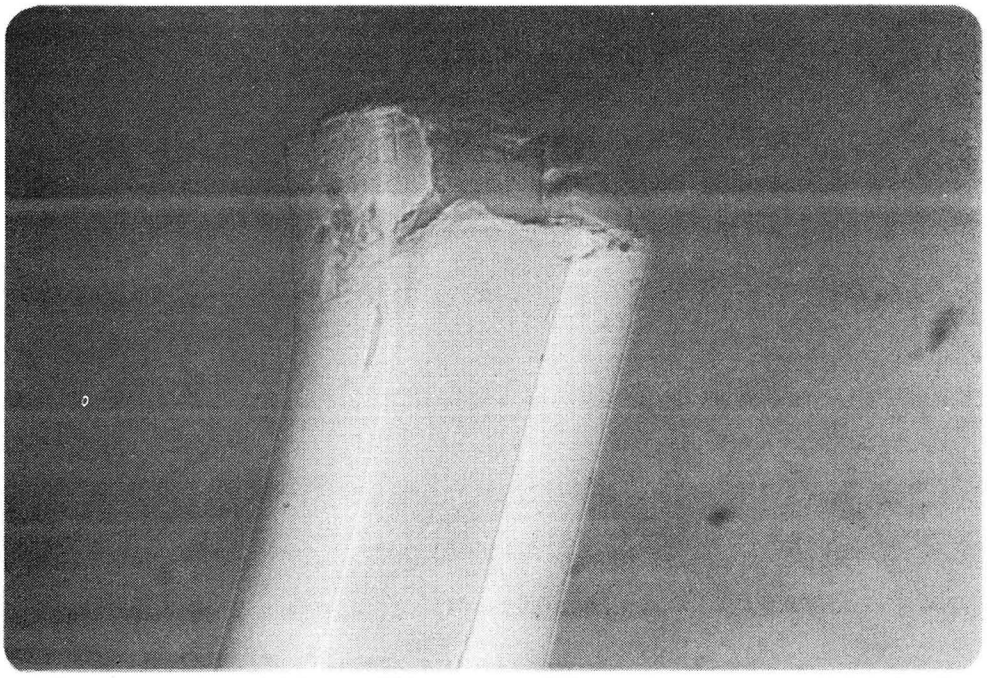


Photo 2 - Hollow fiber soaking in THF saturated with ZnTPP - (50x)

CBB 813-2195

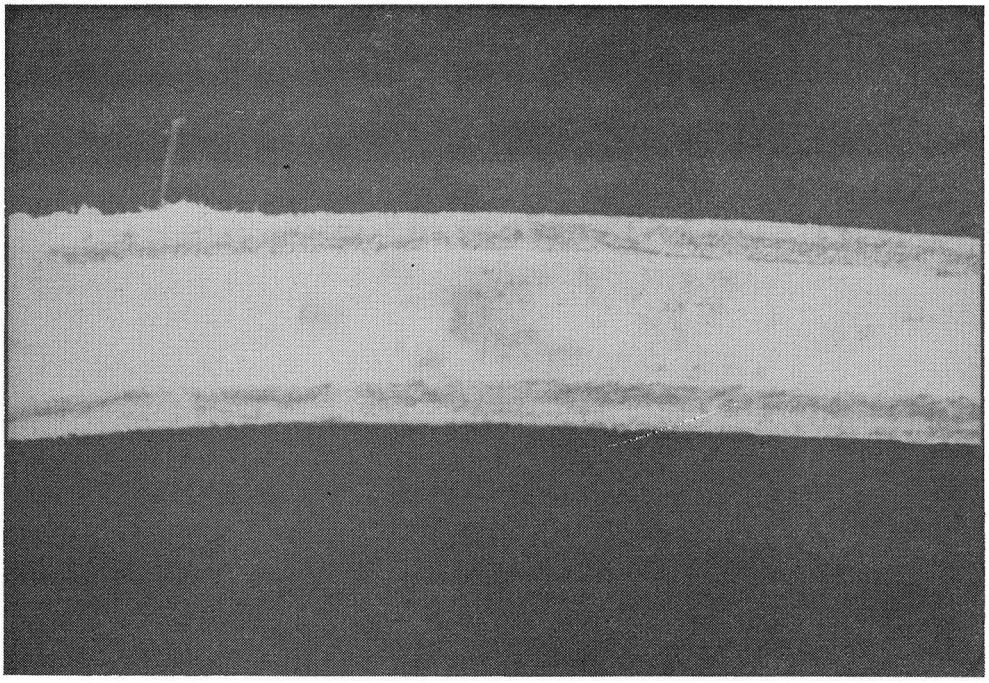


Photo 3 - Treated hollow fiber from
ZnTPP (THF) - (50x)

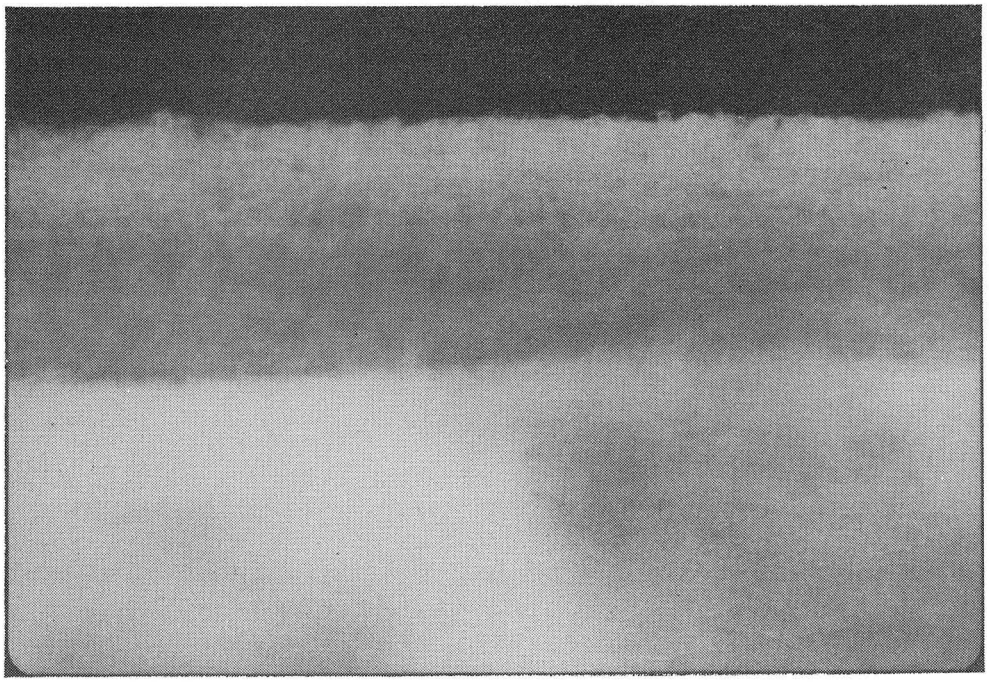


Photo 4 - Treated hollow fiber from
ZnTPP (THF) - (300x)

CBB 813-2199

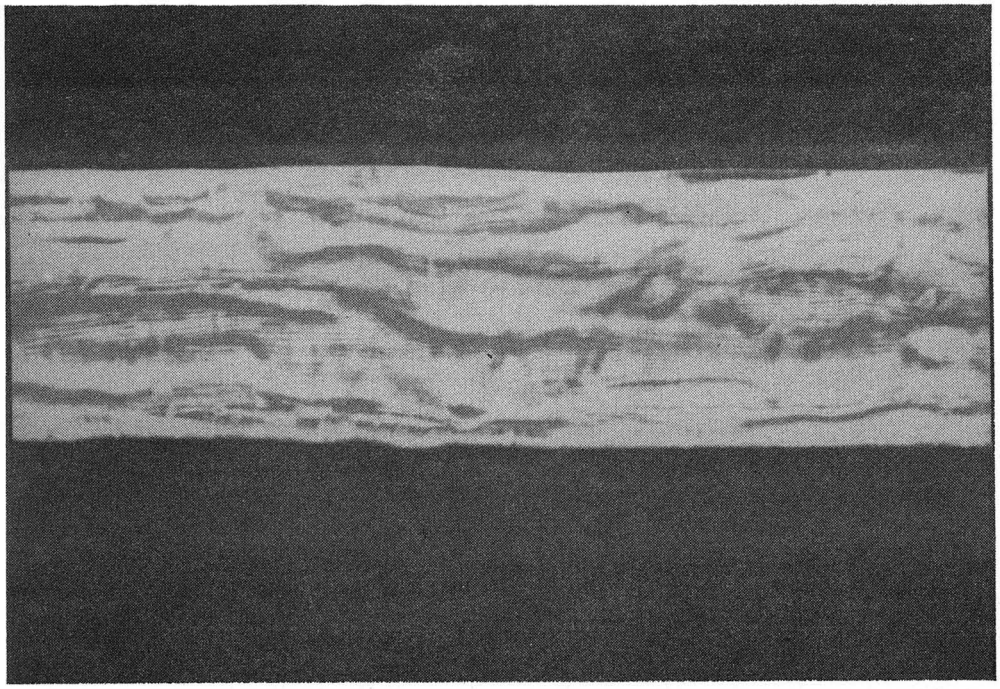


Photo 5 - Treated hollow fiber from ZnTPP (THF), annealed in boiling water - (50x)

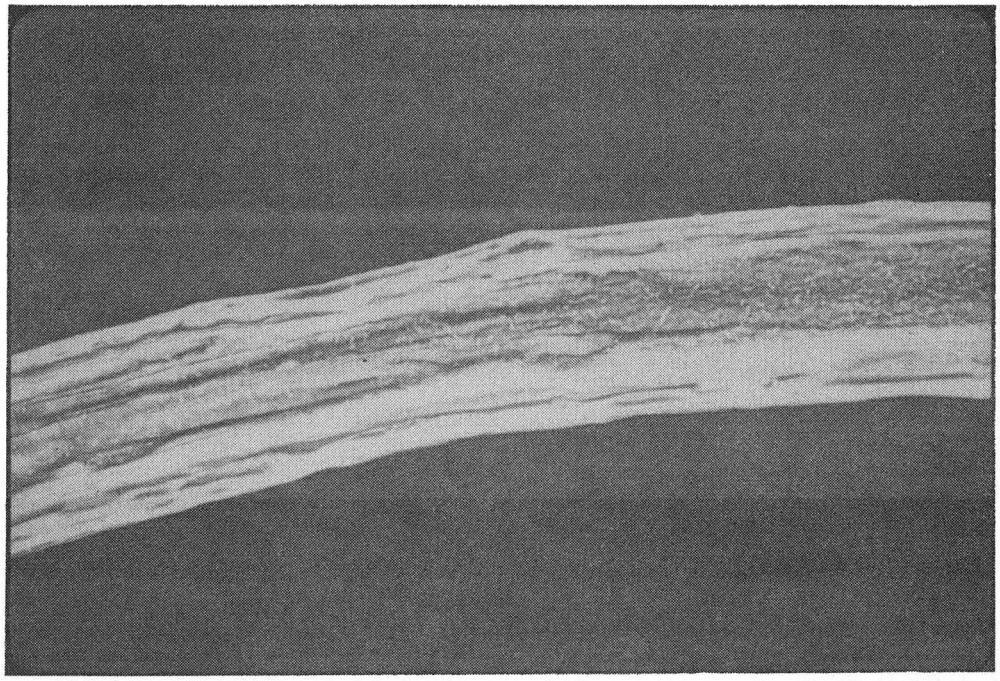


Photo 6 - Treated hollow fiber from ZnTPP (THF) with a THF rinse - (50x)

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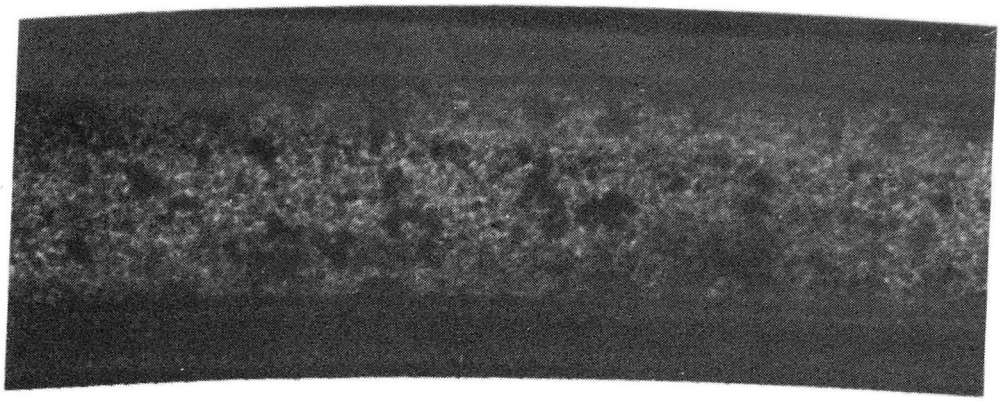

Photo 7 - Treated hollow fiber from ZnTPP (acetone) - (50x)

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