The state of the art of microfiltration

Current and future applications

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A review of micromembrane applications, manufacturing techniques, and anticipated market developments.

The membrane segment of the filtration market has vast potential, but it is still in its relative infancy. In some cases, the infant is growing as the corporate parent gleams with entrepreneurial delight. However, one of the difficulties facing our industry has been the overly optimistic forecasts about our growth rate. The prospect of great expectations has led some companies to exercise careless business judgment.

The key elements for success in a developing or growing market are strong technology/products, superior marketing, and staying power. However, too many in the membrane industry are failing to put their technological advances into perspective with the timing required to penetrate a market or counteract a retaliatory threat from existing competitors or from other new companies with equally eager strategies. The route to market is proving more difficult than anticipated, especially with parallel path developments from a number of suppliers.

In other cases, established market segments appear to have matured, with an overabundance of established suppliers (and capacity) all chasing the same opportunities. These opportunities are expected to explode in volume in "just a couple of years." Unfortunately, this anticipated explosive growth has been just over the horizon for many years now.

These facts notwithstanding, there has probably never been a better time for new companies or products in the membrane market. Although market opportunities are often overstated, the potential rewards for a supplier with a superior product and the financial flexibility to hang tough are great.

Microfiltration rating

Figure 1 illustrates the range of particle sizes over which different filtration processes are capable of operating. The microfiltration segment of this spectrum ranges between 0.1 μm and 10μm (*1*). However, 0.1μm to 5μm encompasses 99% of the applications. The industry routinely refers to microfiltration as "absolute" filtration because this process can achieve filtration efficiencies of 100%. This absolute rating applies mostly to applications below 3μm. Efficiencies slowly erode for particles larger than 3μm, particularly in high-pressure situations.

History of microfiltration

Table I shows the major developments in microfiltration since 1748. The desire to detect microbial contamination in water led to the first meaningful production and commercialization of the microfiltration process in the 1940s and early 1950s. At the end of World War II, the total worldwide market was estimated at about $75,000 (*4*).

In the early 1950s, membranes began to be recognized for their value and commercial potential through the use of microfiltration for air monitoring, laboratory analysis, and diagnostic testing. Then in the mid-1950s and early 1960s, several European and American companies were formed to expand these and other filtration markets, including ultrafiltration in dialysis and reverse osmosis for desalination.

Activity accelerated in the late 1960s and early 1970s when microfiltration technology expanded into several new markets. These included parenteral drug filtration for injectable substances, the manufacture of particle- and bacteria-free rinse water for the emerging semiconductor industry, as well as medical devices such as intravenous filters, burettes, and spike vents. Ultrafiltration and reverse-osmosis applications also found new markets following the development of membranes for food, beverage, and cosmetics as well as gas enrichment and separations.

In the 1980s, several new companies entered a market that had previously been dominated by only three or four major producers. These new players adopted one of two strategies. Some offered conventional products priced to capture market share. The others provided a unique technology for a narrow segment of the market. Most of these firms have not had a large impact on the market. Some were bought out by the majors, while others closed their doors. New companies continue to enter the market, particularly the biotechnology market, which is expected to yield considerable opportunity in the years ahead.

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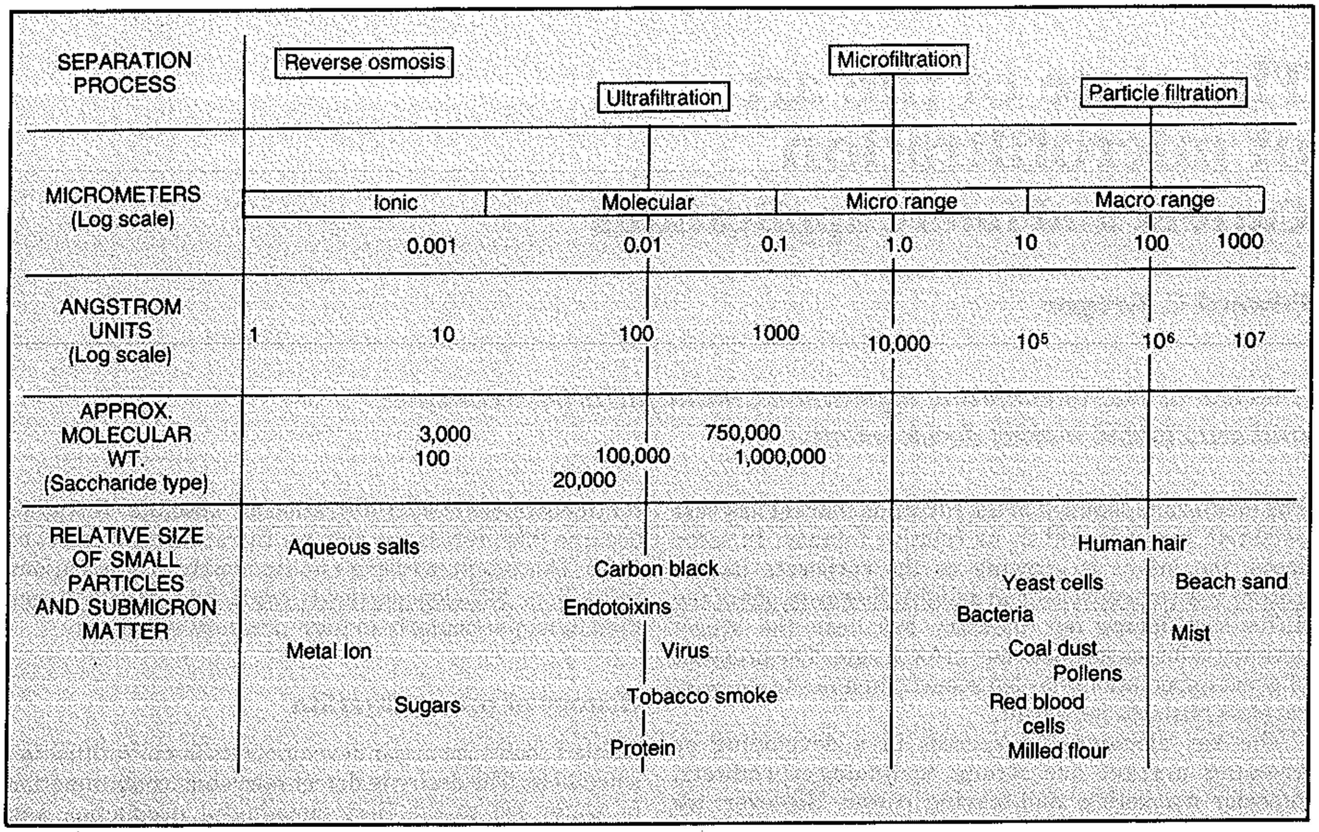
1. This is the range of particle sizes over which four filtration processes are capable of operating. The microfiltration segment of this spectrum ranges between 0.1μ and 10μm. The bottom of the figure shows the relative sizes of various particles. [Figure reproduced from (2).]



Future

The past 25 years have been a time of growth for the membrane market, especially for microfiltration membranes. However, the future appears to hold even larger rewards and, of course, its share of risks.

The 1980s began a new era for microfiltration membranes. Microseparation processes using microfiltration membranes (mostly in submicrometer pore sizes) in high-flow crossflow configurations for traditional filtration applications are proving effective and popular. In addition, micromembranes are being used increasingly in both crossflow and direct-flow configurations for the separation, recovery, and subsequent use of biotechnology components.

Microfiltration membranes in these crossflow configurations have also become increasingly popular with manufacturers of ultrafiltration, reverse-osmosis, and plate-and-frame systems. These systems manufacturers, as well as the traditional microfiltration customers, are discovering numerous advantages in combining high flow rates with long life between element change out. The systems companies are benefiting from new opportunities, while the users enjoy relatively long-term maintenance-free microfiltration.

High-tech markets vs. low-tech, nontraditional, and consumer markets

The future of microfiltration membrane technology is clearly moving in two directions.

High-tech markets. Examples of the high-tech applications include strainer bags with membranes bonded downstream and outside the bag in serial fashion. This technique can eliminate, to a considerable extent, the need for extensive membrane prefiltration, thus offering much-improved cost savings to the user. In time, full-integrity testable systems will be available.

The market for membrane materials with a zeta potential is growing. These materials permit endotoxin removal with much larger pore sizes and high flow characteristics. Transdermal patches utilizing high-molecular-weight drugs may soon be marketed through prescription. This is an extension of the highly popular dense-film transdermal patches used in association with low-molecular-weight drugs such as nitroglycerin. Microporous membranes are also increasingly used as a base substrate for much tighter membranes or thin-film veneers for gas separations or protein separation—two different applications with a common technique.

High efficiency particulate air (HEPA) filtration is already offering an expansive potential for microporous membranes. Users in the semiconductor industry, for example, are demanding Class 10 or even Class 1 clean rooms. Since microporous membranes do not tend to shed as does glass, and with new low-cost membranes only a year or two in the future, HEPA-grade air filtration offers a potential opportunity for significant growth.

Other areas offering new or expanded high-tech markets include robotics and hydraulics. Membranes are also finding use in filtration applications traditionally restricted to depth media. These applications include use in rotary drum filters, vacuum filters, bag-house filters, and filter presses. Goretex is pioneering this area.

I. History of microfiltration

1748	Friar Abbe Nollet: • Osmosis through animal bladders
1855	Fick: • First synthetic membrane (nitrocellulose)
1918	Zsigmondy and Bachmann • Development of commercial process
1927	Sartorious Werkes • Began commercial production
1954	Millipore Corp. • First membrane company formed
1964	Gelman Sciences Inc. • Fabric-reinforced membranes
1970	Celanese Corp. • Polypropylene membrane
1970	W.L. Gore and Assoc. • Expanded PTFE
1984	Gelman Sciences Inc. • Sunbeam process
1984	Pall Corp. • Affinity membranes

Based on information from Porter and Billiet (3).

II. Low-tech, nontraditional, and consumer markets

- Industrial air filtration:
  bag-house filters, HEPA filters, clean-room filters
- Industrial Disposables:
  Clean-room garments, clean-room wipes & gloves, nonmedical packaging, printing/typewriter ribbons, battery separators
- Construction products:
  Housewrap, single-ply roofing, wallpaper
- Military:
  Nuclear, Biological, and Chemical defense garments, tents, masks, gloves & shoes, rainwear
- Agriculture:
  hydroponic farming, herbicide release & weed control, root containers
- Consumer/personal hygiene products:
  diapers, incontinence, feminine hygiene products
- Medical/health-care disposables:
  drapes, gowns, sterile wraps, bandages, wound dressings, packaging for medical & health-care products, transdermal patches
- Consumer durables:
  Nonmilitary outerwear garments (or fabric for such garments), tents, shoes sleeping bags
- Industrial durables:
  bedding, automobile/aircraft applications, automobile covers, sound dampers, protective garments, vapor barriers

III. Value of U.S. membrane markets for the various filtration and separation applications, $ million

	1985	*1990*	*1995*	*2000*
Reverse osmosis	50	70	95	125
Ultrafiltration	56	100	120	165
Dia/Hemodialysis	82	84	86	88
Gas	15	22	46	85
Electrodialysis/Reverse Electrodialysis	15	28	50	80
Microfiltration[a]	165	270	450	670
Subtotal	383	549	847	1213
Microfiltration[b]	105	190	610	1950
Total	488	739	1457	3163

[a]Traditional markets.
[b]Nontraditional (uses include consumer and low-tech markets).

IV. Projected annual growth in U.S. membrane markets (1985-2000)

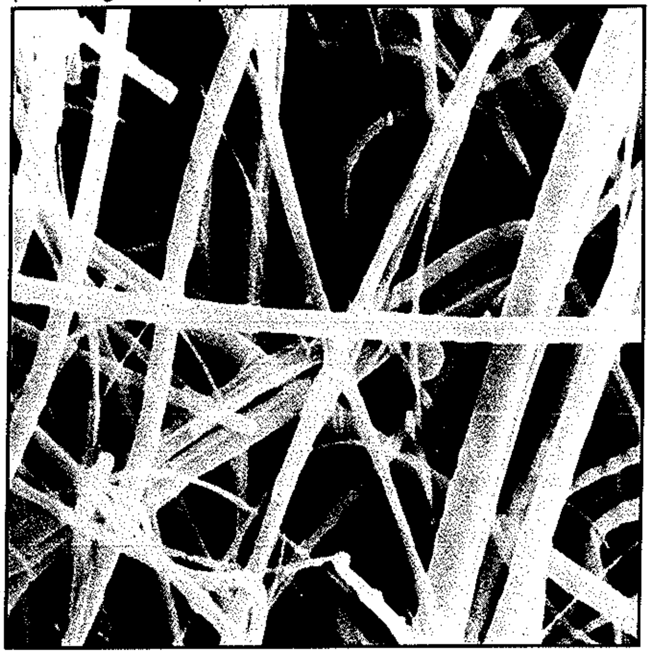
	Annual growth, %
Reverse osmosis	10
Ultrafiltration	14
Dia/Hemodialysis	0.2
Gas	15.6
Electrodialysis/Reverse Electrodialysis	15.4
Microfiltration (traditional)	9.9
Subtotal	7.9
Microfiltration (nontraditional)	21.6
Total	13.8

Finally, perhaps the most sophisticated application for microporous membranes involves the use of their high internal pore surface area as a reaction surface. This includes affinity membranes for the immobilization of protein, including immunoglobulins. These membranes are currently being used as the basis of a new generation of diagnostic test kits. Other chemicals can also be fixed to the internal pore surfaces of these membranes. Such membranes can be used for chromatographic separations, with the separated items then held within the membrane for later recovery. This remarkable application will be used in place of slow and costly methods now used in mass production. This technology is currently seeing an explosion of patents and new companies.

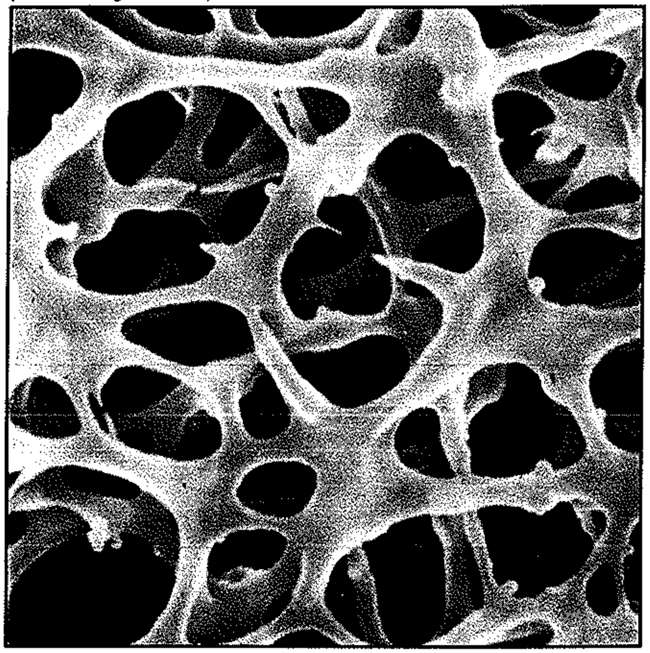
Low-tech, nontraditional, and consumer markets. Recent advances in the manufacture of high-speed, low-cost membranes are expected to affect several cost-conscious markets and applications in the late 1980s. **Table II** lists several of these markets and specific applications, most of them involving the use of a hydrophobic polymer.

The cost penalty (if any) using new lower-cost membranes will be minor compared with the enhanced product performance. As the technology is perfected, these cost-saving membranes and processes are expected to spill over into the traditional microfiltration membrane market which, in turn, will provide new opportunities for expanding the use of membranes in depth-media applications.

2. The matrix structure of depth-filtration media is quite irregular (250X magnification).



3. Micromembrane media have a narrow pore-size distribution (7000X magnification).



V. Comparison of depth filtration and micromembrane filtration

Depth filtration

Advantages:
- High flow rates
- High dirt-holding capacity
- Inexpensive

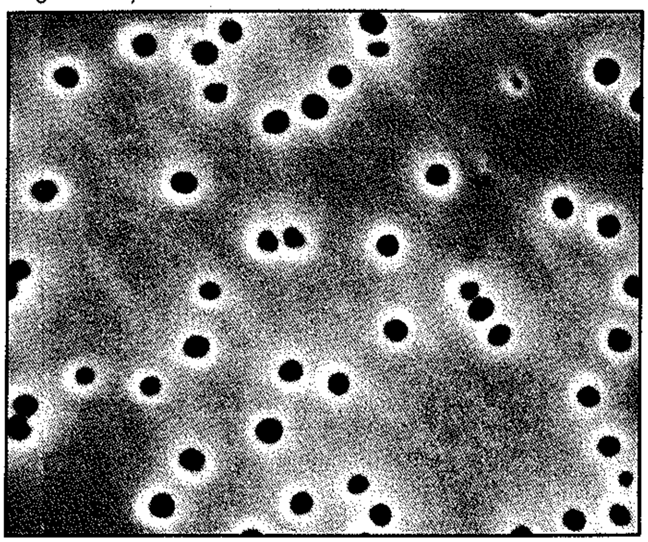
Disadvantages:
- Wide pore-size distribution
- Offloading of particulate
- Media migration
- Leachable binders

Micromembrane filtration

Advantages:
- Absolute filtration
- Narrow pore-size distribution
- No media migration
- Low extractables

Disadvantages:
- Low flow rates
- Poor dirt-holding capacity
- Expensive

4. Nuclepore membranes have clearly defined pores (800X magnification).



Membrane market size and growth rate

The dollar value of the membrane market for the different filtration and separation processes is shown in **Table III** for 1985 to the year 2000. The bulk of the $105 million for the 1985 nontraditional microfiltration market is for Goretex® outerwear and similar nonfiltration applications.

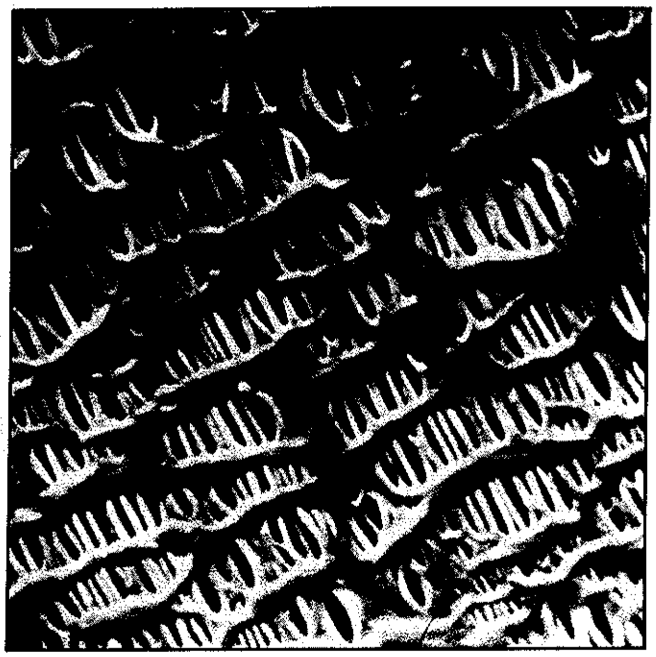
The growth for each of the market segments is shown in five-year increments. The growth in nontraditional microfiltration is of particular interest (*4*). The dollar value of this market segment in 1985 was as large as that for reverse-osmosis and ultrafiltration membranes combined, and it was more than 60% of the traditional microfiltration market. By the year 2000, even with healthy growth from all combined membrane segments, the nontraditional use of membranes will far outpace the other sectors. This advance is being led by some of America's, Europe's, and Japan's largest material suppliers.

Table IV shows the projected annual growth in each of these market segments between 1985 and the turn of the century.

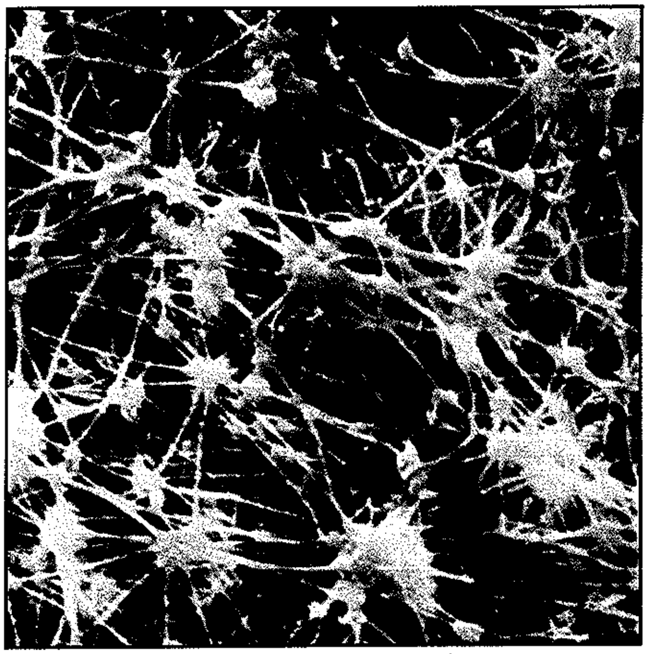
Comparison of filtration media

Micromembranes and depth media are both used in filtration applications, but their modes of operation are very different. **Figure 2** is a photograph of a typical depth-filtration medium. **Figure 3** is a photograph of a typical micromembrane. Depth media have much larger pores and generally serve different markets than micromembranes. The narrow pore-size distribution of micromembranes makes them suitable for surface

5. Celgard® membrane (7000X magnification) (*4*)



6. Goretex® membrane (7000X magnification) (*5*)



filtration applications. Depth media, on the other hand, trap particles within a fiber matrix. **Table V** lists the the advantages and drawbacks of each medium in filtration applications.

Micromembrane formation and construction

The manufacturing techniques used to produce the different microfiltration and microseparation membranes vary widely. However, generally speaking, the function of the finished products are similar. For example, 0.2-μm membranes from different manufacturers have the ability to separate out 0.2-μm particles with extreme efficiency. The differences lie within individual characteristics such as flow rate, chemical compatibility, tensile and tear strength, filter life, and a host of other important considerations, including the ability to fabricate a product from a given medium.

Nucleation track method

The nucleation track (radiation) method of manufacturing membranes was pioneered by General Electric. Starting with polycarbonate (hydrophilic) thin films (1-2 mils), radiation nuclei are passed through the membrane thickness, causing a slight degradation of the film at the point of bombardment. A subsequent chemical wash removes the weakened polymer, leaving straight-through holes of highly defined size (*6*). Nuclepore Corporation is the sole manufacturer of these membranes and maintains less than 1% market share. **Figure 4** is a photograph of a typical membrane manufactured using this technique.

Stretch process

The next most commonly used method for the manufacture of microfiltration membranes was popularized in the early 1970s by Celanese Corp. (Celgard®) and W. L. Gore and Associates (Goretex®). Each uses a method based on stretching a polymer film such as polypropylene (Celgard) or Teflon®-polytetrafluoroethylene (PTFE) (Goretex) to form the pores (*7*). Both Celgard and Goretex membranes are 1-2 mils thick with hydrophobic characteristics. Both can render their materials wettable through the use of surfactants.

These two companies have been highly successful, particularly in nonfiltration applications. Celgard is used for battery separators, blood oxygenation, and mushroom-bag vents. Goretex is used in outerwear products. Celgard and Goretex membranes are illustrated in **Figs. 5** and **6**, respectively.

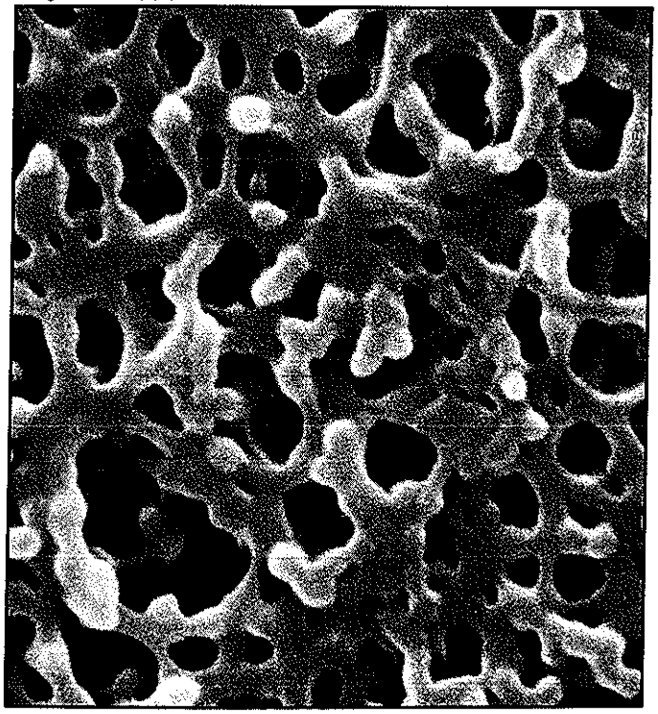
Together, these two companies compose about 10% of the microfiltration membrane market, with the overwhelming advantage to W. L. Gore and Associates, which is using the Goretex membrane in fabrication of bag-house filter bags and rotary-drum filter blankets. In the absence of meaningful competition, Gore and Associates could dramatically increase its share of the filtration market in the next year or two.

Wet-cast process

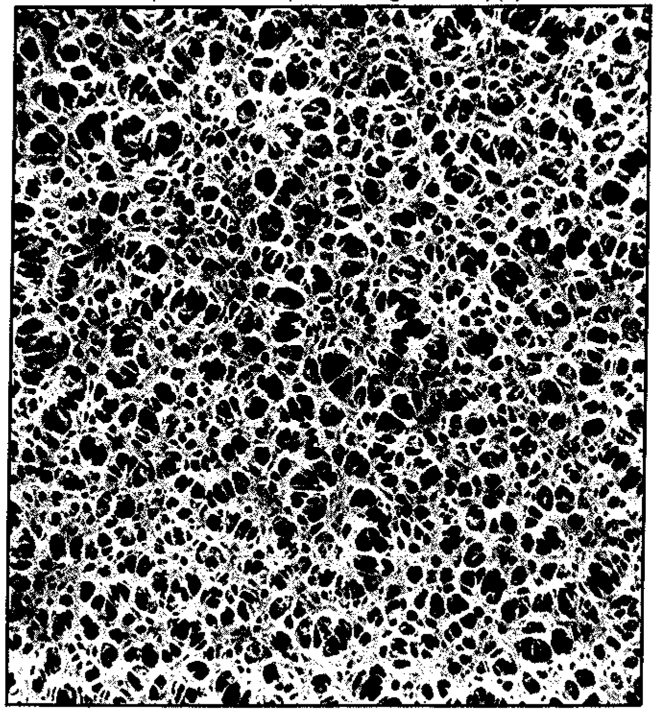
The oldest and most commonly used method of manufacturing membranes is the wet-cast process. This method is used by the major suppliers: Gelman Sciences, Millipore Corp., Pall Corp., and Sartorius. With about 90% market share, these manufacturers use a diverse range of polymers to form their membranes. The most common are from acrylic, cellulose, nylon, polyvinylidene difluoride (PVDF), polypropylene, and polysulfone polymers.

The wet-cast manufacturing technique varies slightly from manufacturer to manufacturer. However, the basic principle involves dissolution of a polymer in a solvent and a nonsolvent. After re-formation of the polymer by removal of the solvent, the nonsolvent (pore former) is extracted through a washing stage, leaving a membrane construction with tortuous pathways. Membrane thickness is 3-8 mils, depending on whether the

7. Wet-cast membrane with nonwoven-fabric reinforcement (800X magnification) (6)



8. Membrane manufactured by high-speed Sunbeam process has a well-defined pore structure (7000X magnification) (7).



membrane has a fabric reinforcement (*8*). All manufacturers offer both hydrophilic and hydrophobic versions of their products. **Figure** 7 illustrates a wet-cast membrane with nonwoven fabric reinforcement.

High-speed process

At least one manufacturer, with others likely to follow, has developed a high-speed, low-cost process for manufacturing micromembranes. Conventional processes generally manufacture membranes at 5–15 ft/min at widths ranging from 12 in. to 36 in. The Sunbeam process™ is expected to yield 60–96-in. webs at 350–600 ft/min when fully scaled up within the next three years (*9*). **Figure** 8 illustrates a membrane manufactured using this process.

The Sunbeam process creates membrane structures through the crosslinking of monomers and oligomers under either an ultraviolet or electron-beam source. Twelve-inch prototype materials are now available in both hydrophilic and hydrophobic grades as films or as 2–4-mil-thick composites supported with nonwoven fabrics. Forty-inch widths will be available from a semi-commercial facility in July 1988.

This process is expected to provide access to the consumer markets listed in Table II. Depending on volume and membrane construction, it should yield membranes up to 10–15 times less expensive than the membranes that are now being manufactured (*9*).

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