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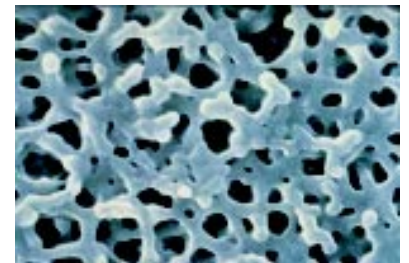
Primer on Membrane Filtration

Description:

Polymeric membranes are classified in broad categories by their ability to remove particles, ions and other substances by size. Microfiltration (MF) removes particles from approximately 0.05 to 10 micron, Ultrafiltration (UF) passes salt ions, but retains particles and large dissolved molecules (>1,000 molecular weight or >30 angstrom), Nanofiltration (NF) typically has partial salt retention and rejects solutes in the 300 to 2,000 molecular weight range with separations of 10 to 30 angstroms and Reverse Osmosis (RO), below 10 angstroms and usually is defined as near complete removal of salt ions. MF and UF membranes have visible pores under high magnification. NF and RO membranes do not have holes as such, but rely on high pressure to defuse a liquid or gas through the molecular structure of the medium by absorption/desorption through the membrane. The molecular weight is carefully controlled creating membranes designed to have a desired molecular cut-off (MWCO) level. The MWCO number defines a specific particle size unable to permeate a NF or RO membrane.

The Freedonia Group, Inc., in the past has reported the demand domestic for membranes in millions of dollars as:

	<u>2006</u>	<u>2011</u>
Total Membrane Demand	2,110	2,940
Microfiltration	980	1,290
Reverse Osmosis	490	740
Ultrafiltration	420	630
Pervaporation	65	95
Other	155	185



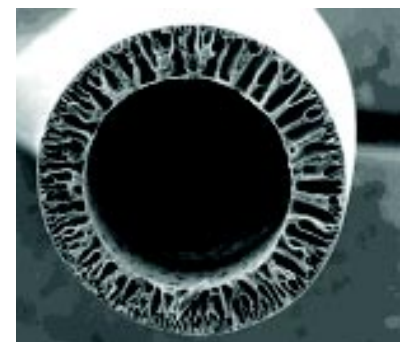
Microporous Membrane 5000 Magnification



Microfiltration Cartridges with Various End-Caps

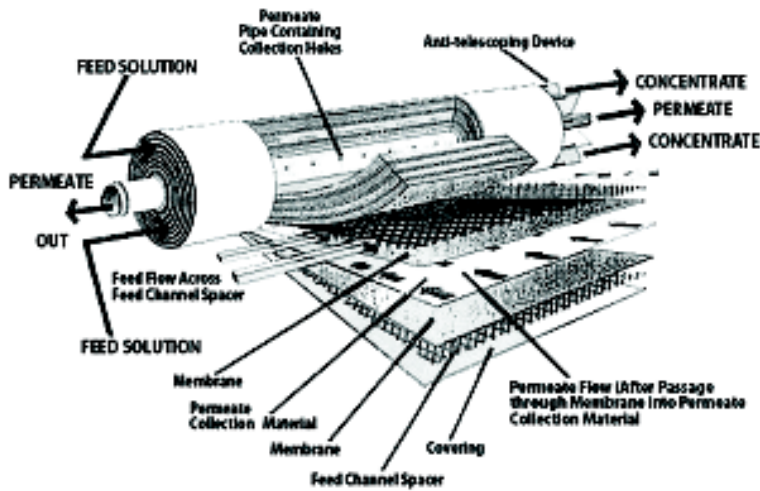
Other studies report both higher and lower market size. Assuming the Freedonia 2006 number is reasonably accurate, the growth is extremely conservative for 2011, in my opinion. The 2011 numbers, especially for MF and RO are likely under-estimated and will be 25 percent or perhaps higher than shown. Dramatically influencing this accelerating growth is a growth market with few boundaries related specifically to water and water re-use among other needs. This growth includes the removal of vast quantities water from every gallon of oil during oil drilling operations, referred as produced water. Produced water, contains particulate and chemicals such as toluene, xylene and benzene. Refinery gas streams include hydrogen sulfide and ammonia, which needs to be filtered and/or coalesced before discharge back in to the ground or into rivers or lakes. Other examples of industries with process discharge requirements using immense quantities of purified water include the paper-making industry, electrical power generation from nuclear and coal fired power plants and treatment of municipal sludge to name a few. On the other hand, make-up water for beverages for soft drinks requires enormous quantities of purified potable water prior to its use, rather than discharge clean-up. Membranes and their associated systems growth will explode even further in the future with the overwhelming need potable water including irrigation for farming in many arid regions of the world and including areas west of the Rocky Mountains in the United States.

Selling prices for MF membranes range from \$3.00 to \$6.00 a square foot. There are exceptions at both ends of the range, but vast majority of performance rated mem-



Hollow Fiber Membrane

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Spiral Wrap Module Schematic

branes fall in this range. RO/NF membranes vary widely depending upon volume, molecular weight cut-off and other factors. There majority RO/NF membranes sell under \$1.00 per square foot with some situations as much as \$2.00 per square foot in special circumstance application. Pricing is largely a factor of volume and the end-uses applications.

History:

Membranes have two basic and independent histories. Microporous membranes became commercial in Germany in small quantities prior to WW II. Reverse Osmosis membranes were originally developed, from cellulose acetate, in the early 1960's at the University of California as a means to desalinate seawater. The late 1960's and 70's saw the formation of most of today's best-known and largest membrane manufacturing companies.

Manufacturing Methods:

Most membranes are made using a wet-casting process. Pores are generally created, in the case of MF and UF membranes, when a solvent evaporates leaving the polymer to form around a "pore-former" which is subsequently extracted through a washing step. NF and RO membranes form a structure based on the molecular makeup of the polymer during the casting (spinning), gelation and drying stages. Bi-axially stretched MF membranes from PTFE and polypropylene polymers are formed when a film is bi-axially stretched causing pores to form during a controlled stretching process. Track-etch MF membranes are formed when thin polymeric films, such as polycarbonate, are bombarded with fission fragments to form tracks, which are subsequently chemically etched to form pores. Track-Etch membranes have less than 1 percent market share.

Material(s) of Construction:

Typically, microporous membranes are made using many polymers. The most popular being nylon, PVDF, polyethersulfone

and PTFE. UF, NF and RO membranes are usually constructed from the polymers; polyethersulfone, cellulose acetate, PVDF and in some cases polypropylene.

Media Forms:

Wet-cast and bi-axially stretched microporous membranes are manufactured as flat roll stock usually in the general range of 125 microns thick. Bi-axially stretched membranes are approximately 25 microns thick. MF membranes are manufactured as both unsupported films and coated or laminated to nonwoven reinforcements. UF, NF and RO membranes are supplied as fabric reinforced roll stock for both spiral wound modules generally for liquid use and as hollow fiber tubes (straw-like) with porous walls capable of permitting liquid and/or gas fluid transfer and separations. The flow (flux) is either from outside-in or inside-out of the hollow fiber wall.

Special Characteristics:

Membranes commonly have a narrow pore size distribution especially in the case of MF and UF membranes, where as the molecular weight cut-off for NF and RO membranes are a bit wider due to the difficulty in controlling the reaction and molecular weight spacing that forms the pore structure and MWCO. Membranes in all categories are considered to be a surface filter media, in that particulate does not tend to collect within the cross-section of the media, but on the upstream surface. As a result, membranes require a fairly clean feed stream with low concentrations of contaminate. Otherwise, they will rapidly blind over with particulate and greatly restrict or shutdown fluid flow/flux.

Filter Configurations and Function:

MF membranes are typically pleated loosely with spunbonded nonwoven fabric support and incorporated into cartridges, or die cut into flat parts used in small parts such as vents in medical devices or small filters in injection molded plastic housings. UF, NF and RO flat stock membranes are almost always spiral wrapped and configured into 40" long cylindrical modules, although certain microelectronics cartridges are beginning to use UF membranes in large diameter pleated cartridges. Another means to filter fine particulate and ions is via narrow diameter hollow fiber membranes. The membranes packed in parallel as bundles into cylinders and operate in a cross-flow fashion akin to spiral wrap modules. A small cross-flow membrane market consists of larger diameter tubes of ¼ to 1 inch common to the process market for wastewater and food and beverage. Fluid flow for MF is almost always perpendicular or "dead-ended" to the position of the

membrane with particulate collecting on the surface of the membrane. Whereas, in UF, NF and RO, feed stream flow is parallel to the surface of the membrane as the fluid and particulate "sweep" the membrane surface. In this case, particles constantly transverse the surface and carried away in the majority of the feed stream, while the purified fluid penetrates the membrane. Permeate flow is referred to as "flux" in the case of spiral wrap modules or hollow fiber bundles. Feed pressure for MF Cartridges are typically from a few PSI to 20-30 PSI with flow rates measured in liters per minute. UF, NF and RO have very tight molecular structures and are operated up from 50 to several hundred PSI with flux rates measured in a relatively low number of gallons per square meter of membranes surface area per day. Because of these relatively low flow rates UF, NF and RO filters are usually found as large process industry systems, whereas MF membrane filter in single pleated cartridges are fitted into housings, although multi-cartridge housings are not uncommon for large process industry uses.

Market/Applications:

Applications for MF membranes are generally used as pleated liquid filter elements for fine filtration such as water, chemicals and other liquids for the pharmaceutical, medical devices, microelectronics, chemical industries to name a few examples. MF membranes are meant as sterilizing filters to remove bacteria and the finest of particulate in both liquids and air. MF membrane cartridges also serve as air vents in pharmaceutical tanks. In medical and laboratory applications MF membranes are often used in flat form, fitted into filter holders or insert molded with plastic frames and housings. In recent years MF membranes are being used widely in membrane bio-reactors (MBR) in the purification of municipal sledge prior to discharge back into the environment. Other times, MF membranes are laminated to nonwoven fabrics for use in baghouse air filters. UF, NF and RO flat membranes are configured into spiral wound modules or as hollow fiber bundles or larger diameter tubes and part of a large integrated systems. These large systems are used when extraordinary purity is required such as in the semiconductor, pharmaceutical, food and beverage and in waste water treatment discharges applications and in the case of RO for sea water desalination. Hollow fiber membranes are configured into housings and frequently used for a number of applications, including hemodialysis, blood oxygenation and in laboratory separations as well as wastewater recovery.

Advantages:

The primary advantage of MF membranes, at is their ability to be manufactured with highly repeatable and narrow pore size distributions, especially below 1 micron mean flow pore (MFP) rating or as absolute rated membranes at or below

0.45 micron. UF, NF and RO membranes work by virtue of their molecular weight cut-off rating as described earlier.

Disadvantages:

Being surface filters membranes require relatively clean feed streams in liquid applications to prevent rapid fouling. UF, NF and RO membranes tend to have a long life cycle by virtue of their crossflow configuration which "sweeps" away particles. However, they also can blind-over with excessive particulate or in time with an excessive build-up of contaminate. In these cases the membranes can be cleaned through the use of chemicals, backwashed or even backpulsed. Above 0.45 micron pore size, MF membranes loose their absolute liquid rating capabilities and other media such as calendered melt blown fabrics become the material of choice. MF membranes and larger diameter tubular, in particular are expensive on a square foot basis compared to many other filtration media, including UF, NF and RO membranes. The average realized price is in the \$10 to 80 per square yard range depending on the membrane selected and its required end-use. Ceramic membranes are such a small part of the market they are not covered here, other to say they are extraordinarily expensive.

Market Penetration and Trends:

Membranes have made many inroads into the market, especially in the 1970's and 80's. Today, there have been many refinements with growth exploding. Refinements combined with market needs have permitted many new uses especially with MF and UF membranes in biopharmaceutical, medical devices, water and wastewater purification, the microelectronics industry as microchip manufacturing continues its expansion now requiring filtration to wafers and chips with nanometer size features. MF, UF, NF and RO membranes will continue to have enormous growth in the coming years. The world has increasing requirements for ultrapure water, food and beverage and in the treatment of commercial and industrial waste, in addition to many other markets. Legislation by local, State and Federal authorities has and will accelerate the expanded use and need for membranes and membrane systems far into the future. There is no doubt that expanded filtration needs and regulations have made membrane filtration a growth industry.

The foregoing addresses the most common membrane media and certain specialty versions and applications. However, there are too many niche membranes and applications to include in this brief primer.

Edward C. Gregor, Edward C. Gregor & Associates, LLC, Charlotte, NC is a specialist in bring new technologies to market and merger and acquisition services in the filtration, textile fiber and specialty polymer industries.