
수처리용 역삼투막 제조

임 대 우 소장

((주)새한)

Reverse osmosis membrane for Water treatment

D.W.Ihm, K.I.Kim, Y.S.Yoon
Saehan Industries Inc. R & D center

It is known that various dissolved substances or solutes can be separated from their liquids or solvents by various useful separation process or techniques known as ultrafiltration or reverse osmosis. Especially, reverse osmosis membranes are high permeability barriers. For example, in a liquid-liquid system, reverse osmosis membranes have high permeability for water yet are impermeable to micro-organisms, colloidal particles, salts and organic materials, so that these solutes or undesirable materials can be removed.

Reverse osmosis technology, which is generally applied to separation of solutes with a size of 10 Å or less, is sufficient for the desalination of sea water, contaminated water or saline, to obtain pure water for drink or other uses. That is the use of this technology which has apparently gained the widest attention to date is the desalination of brakish water or sea water to provide large volumes of relatively non-salty water for industrial, agricultural, or home use.

Purification of water through reverse osmosis membrane is accomplished by applying pressure to the sea water or contaminated water to force the water through the reverse osmosis membrane, so that purified water passes through the membrane and the salty or contaminant is rejected.

With regard to the characteristics of reverse osmosis membrane, first, it should have high salt rejection coefficient. For commercial practicality, it is required salt rejection capabilities of 98% or more. In addition, the reverse osmosis membrane should permit high fluxes at reasonable pressures in a view of economy.

Ever since John E Cadotte invented FT-30 composite membrane in 1981, the polyamide composite reverse osmosis membranes have been the standard of the RO industries because the TFC(thin film composite) type membrane have shown higher salt rejection, higher flux, and more compaction resistance than the commercial CA(cellulose acetate) membranes. But in recent years, RO industries wanted to have higher flux than the current TFC membranes, since employment

of high flux membranes operating at lower pressure, could save operating cost(electricity).

Saehan industry developed composite type RO membrane in 1994. In this article we introduce the characteristics, process of making the RO membrane and recent research development of RO membrane

수처리용 역삼투막 제조 (Reverse osmosis membrane for Water treatment)

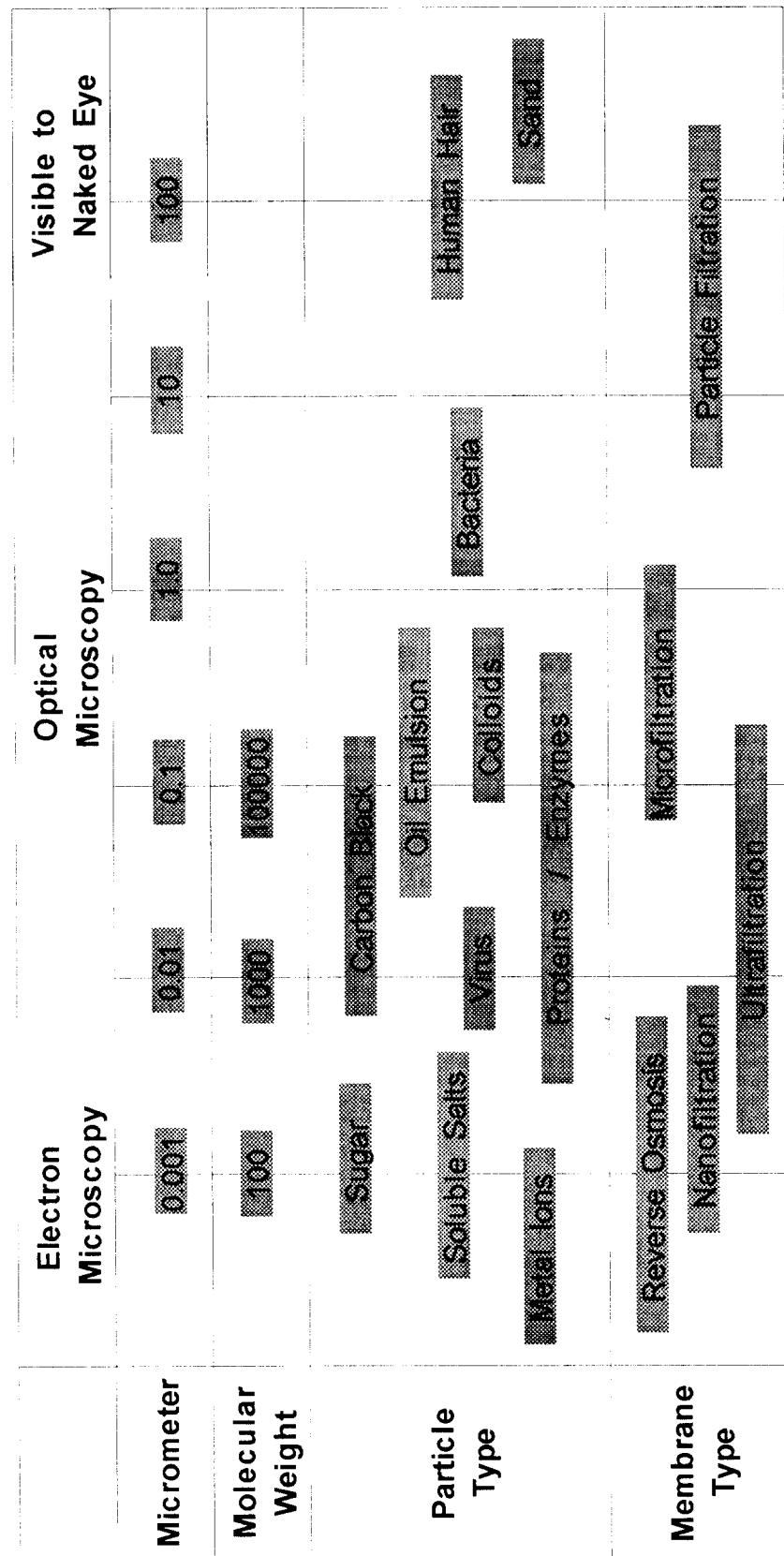
산업발전에 따라 발생하는 각종 오염물질에 의한 양질의 물 부족현상을 해결하거나 산업적으로 특정물질을 분리하기 위하여 새로운 분리기술이 개발되고 있으며 이는 앞으로 인류에 대한 가장 절실한 기술로 떠오를 것이다.

이러한 측면에서 분리막은 가장 효율적인 분리기술로 여겨져 지난 30년간 눈부신 발전을 해왔고 최근 국내에서도 소재개발과 함께 이를 응용한 분리막 System개발이 활발히 이루어지고 있다.

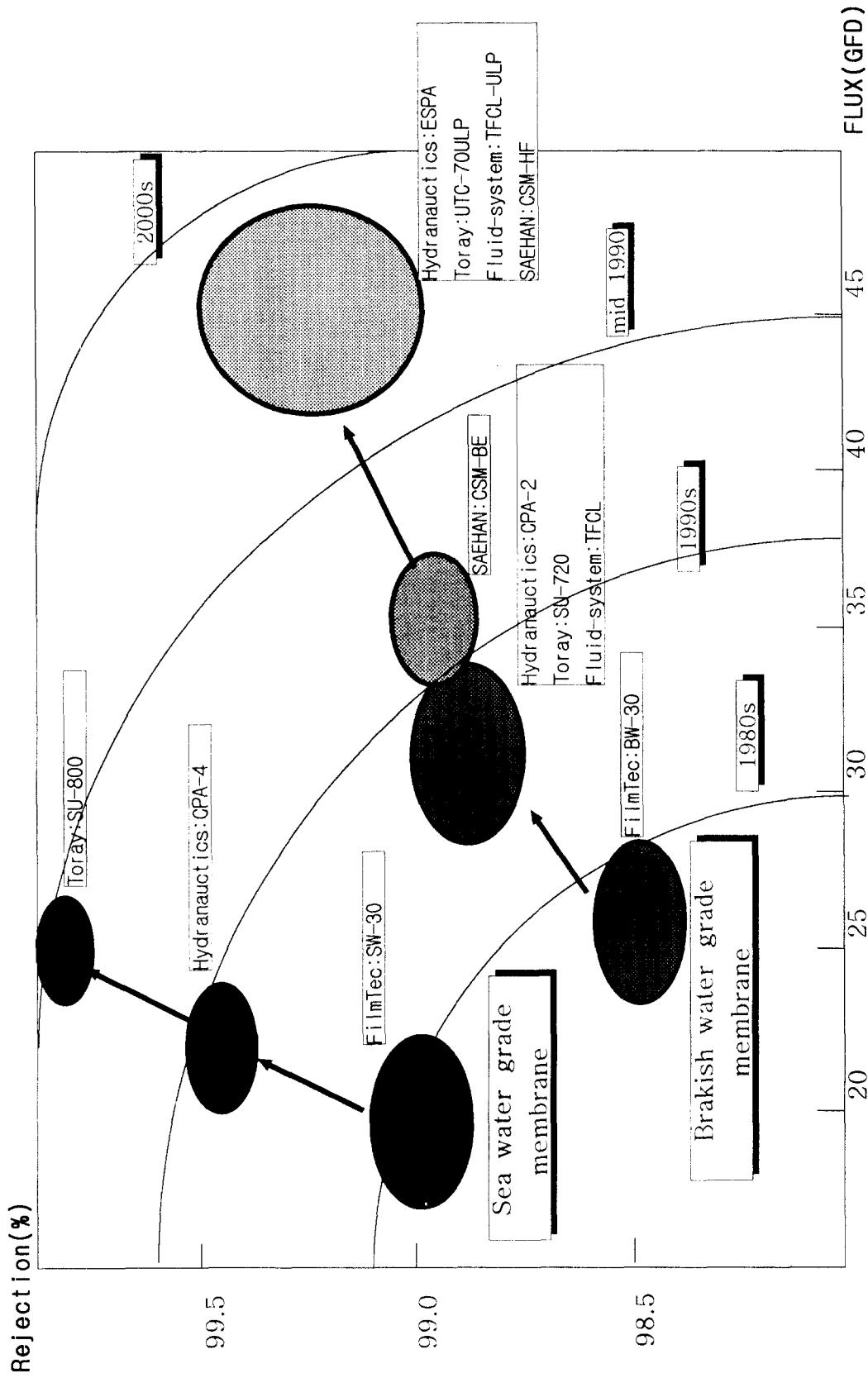
분리막에 의한 공정은 상변화가 없는 분리공정이므로 에너지 측면에서 효율적이며 공정자체가 간단하여 점차 보편적인 기술로 자리를 잡아가고 그 기본원료가 부직포, 중공사나 장단섬유이므로 주로 화성회사 위주로 소재개발이 주로 되고 있다.

본 발표에서는 최근에 국내에서 생산되기 시작한 역삼투막의 제조 방법과 특성 및 개발동향을 총괄적으로 소개하고자 한다.

General Filtration Spectrum



The developmental history of R/O Membrane



Products List

Grade Name	Hydranautics	NTR series (Nitto Denko)	TFC	Fluid Systems
DOW	TW-30, BW-30, SW-30 NF-45, NF-75	CPA-2, CPA-3, CPA-4 SWC, PVDF ESPA	SU-620, SU-720, SU-820	TORAY
		NTR series (Nitto Denko)	TFCL series	SAEHAN
				CSM-RE(B), CSM-RE(L), CSM-RE(S) CSM-NE, CSM-UE

R/O Membrane Material History

● Diacetate Membrane

- Compaction Deterioration in presence of microorganism
- Good Flux (15 GFD)

● Triacetic

- High Salt Rejection, more stable
- Low Flux (3 GFD)

● Blend

- Optimizes DI- and TRI Acetate properties

● Polyamide

- Inert, Wide pH and Temperature range

● Thin Film Composite

- Solution deposition or in-situ interfacial polymerization
- High Rejection, Excellent Flux, stable

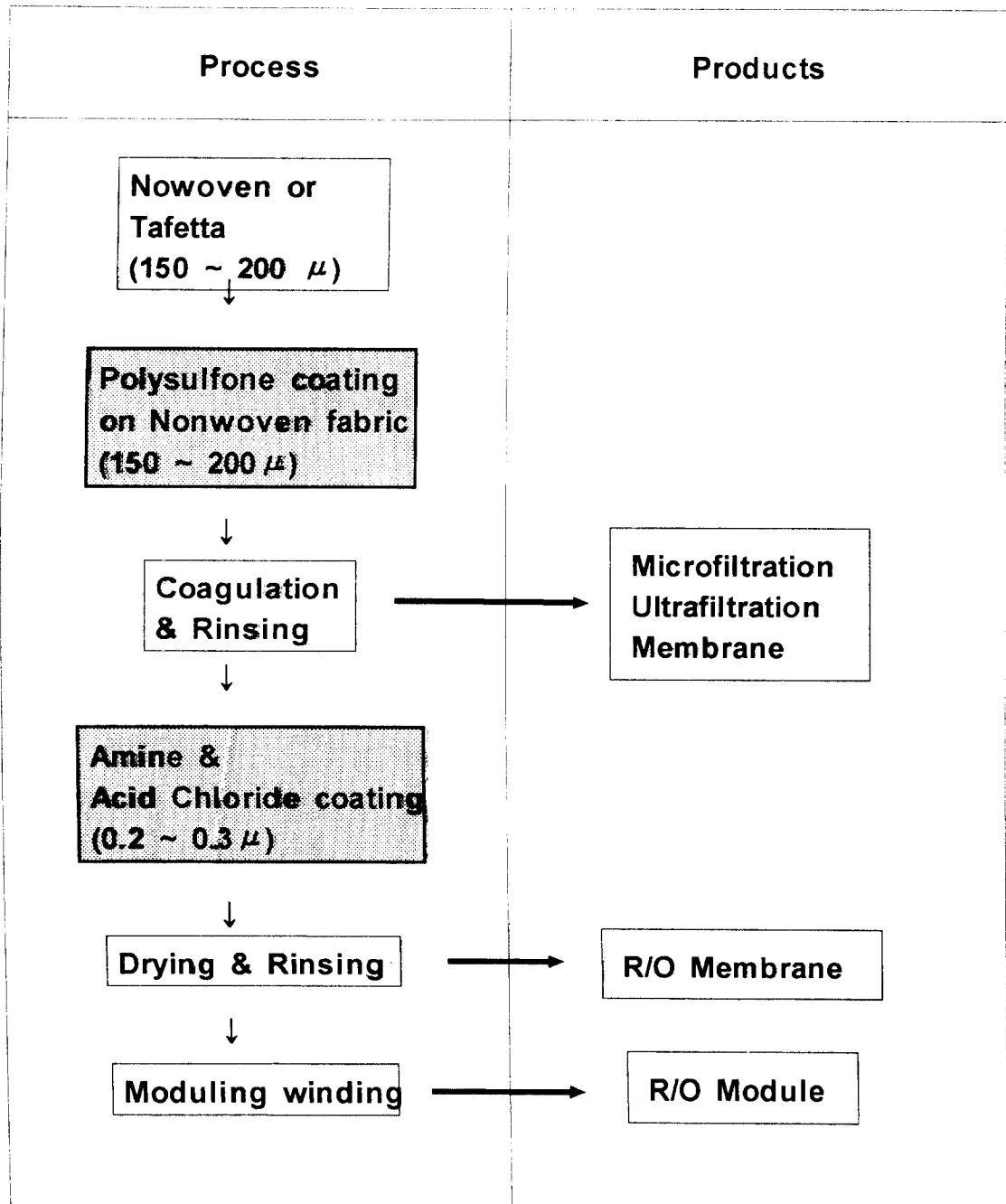
Routes to Composite Membrane

- Cast an ultrathin dense membrane film separately, then laminate to a microporous support
- Interfacially polymerize a reactive set of membranes at the surface of a microporous support
- Dip-coat a solution of a polymer onto a microporous support and dry in place
- Dip-coat a solution of a reactive monomer or prepolymer onto a microporous support followed by a post-cure with heat or irradiator
- Deposit a barrier film directly from a gaseous phase monomer plasma

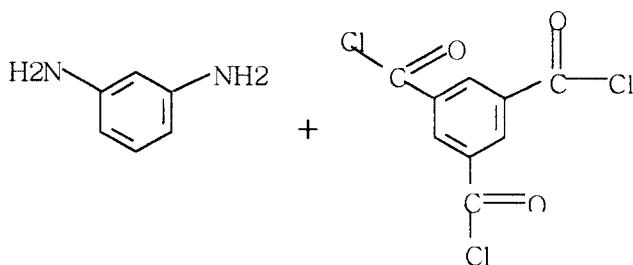
History of R/O membrane

Year	Events	
1959	◎Reid & Breton : Demonstration of desalination capability of cellulose acetate film	
1962	◎Loeb & Sourirajan : Development of asymmetric cellulose acetate reverse osmosis membrane	
1963	◎Riley,Lonsdale : Elucidation of assymmetric CA membrane structure adn identification of solution-diffusion model of transport	
1964	◎Francis : Cellulose acetate thin film composite membrane concept	
1972	◎John. Cadotte : Interfacially synthesized thin film composite membrane NS-100 (PEI + TDI)	
1978	◎John. Cadotte (US patent 4,277,3440): Fully aromatic polyamide thin film composite membrane	North Star R&D Institute
1982	◎Filmtec (J. Cadotte) Marketed "FT-30"	R : 98% FLUX : 25 GFD
1992	◎DOW : Lost the right of US patent 4,277,344 in lawsuit between Hydranautics,Fluid-systems.	
1995	◎Hydranautics : Marketed High flux membrane "ES-10"	R : 99% FLUX : 45 GFD

Manufacturing process of TFC R/O



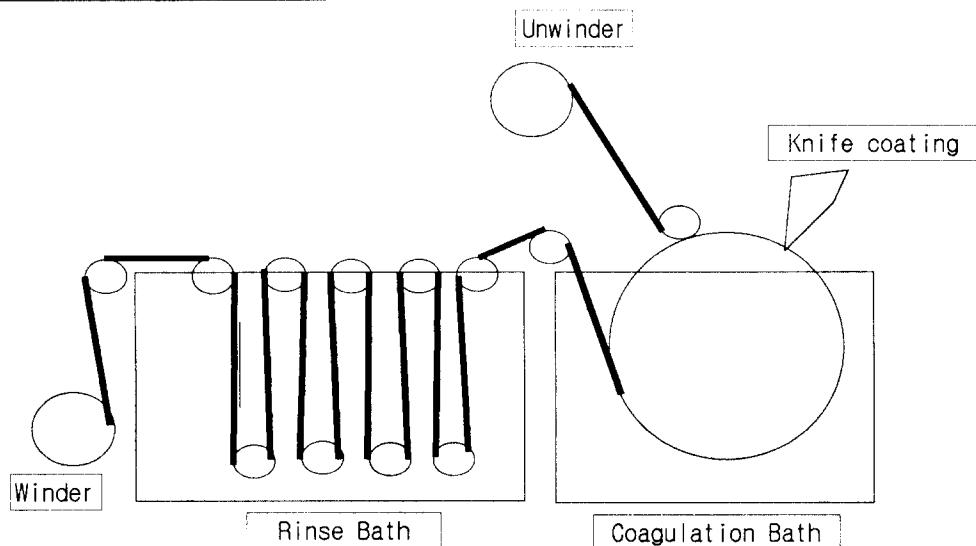
"C S M" Basic Chemistry & Process Variables



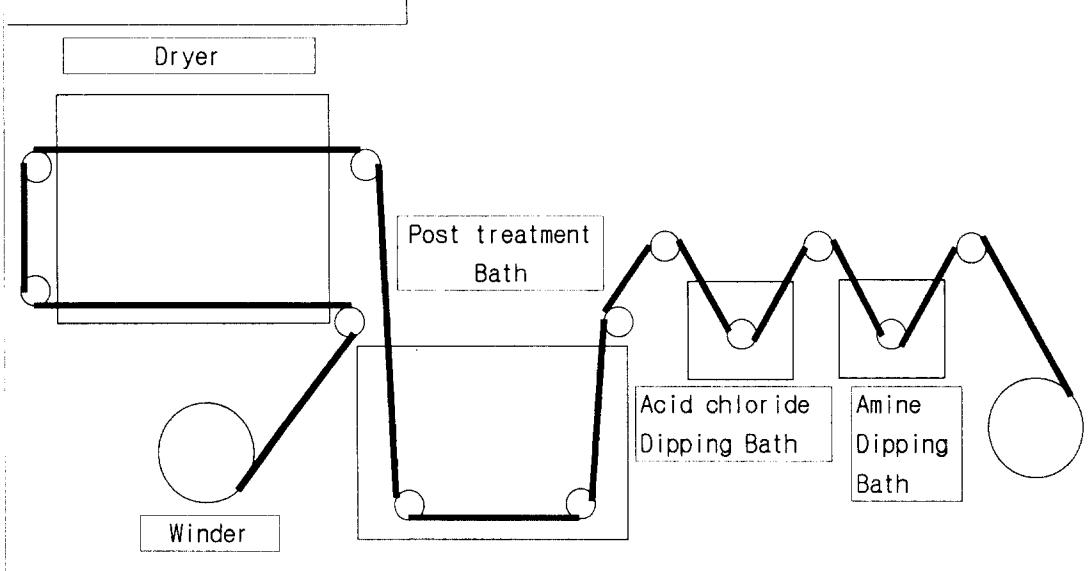
- Properties of porous support membrane
 - Polymer concentration
 - Humidity
 - Surface pore size, distribution and uniformity
 - Wetting characteristics
 - Residual surface water and solvent
 - Substrate tightness
- Amine solution
 - Solubility in solvent
 - Concentration
 - Additive compatibility (wetting agent, acid acceptors)
 - Coating characteristics
- Acid chloride solution
 - Solubility in solvent
 - Stability
 - Reactivity
 - pH
 - Concentration

Concept of Manufacturing process

Casting M/C



Thin Film Coater



New Membrane Research Activities

- High Flux Membranes
- High Rejection Membranes
- Chlorine Resistance Membranes
- Bio Fouling Resistance Membranes



- New amine & new acid chloride synthesis
- Existing amine & acid chloride reaction
 - Additive addition
 - Rinsing
- Post-treatment after coating

Comparison of R/O companies

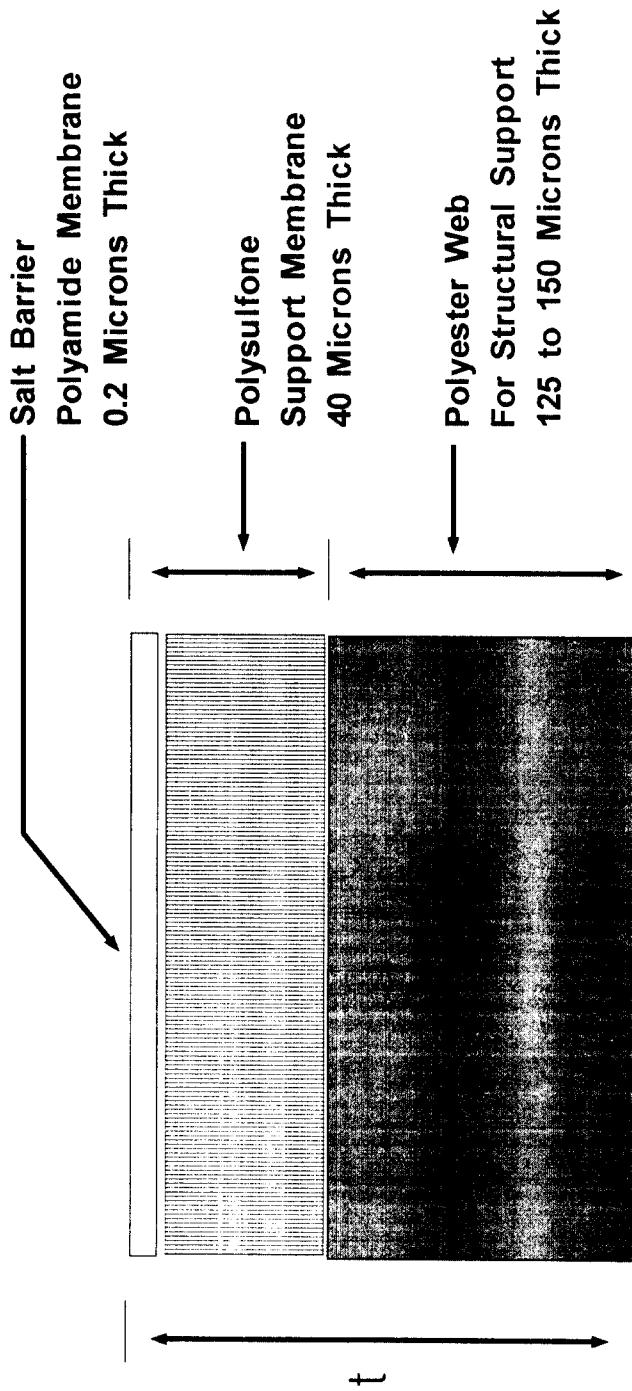
Key researcher*	FilmTec	Hydranautics	Toray	Fluid System	Desalination /Osmonics	Saehan
	John E. Cadotte	J.Tomaschke	Dr.Kurihara	Dr.Chan	Mr. Tombray	MPD+TMC+ Post treat't
Basic Chemistry**	MPD+TMC	MPD/Salt+ TMC/IPC	MPD+TAB +TMC	MPD+TMC+ Citric acid post treat't	-	-
Property ***						
(BW grade)					99.5 ↑	99.0 ↑
Rejection(%)	99 ↑	99 ↑	23 ↑	25 ↑	25 ↑	25 ↑
Flux (GFD) at 225psi,2000 ppm	25 ↑	25 ↑				

註)※) Retired person may be included.

※※) This information obtained from patents

※※※) Some data got from brochure or measured from marketed sample by Saehan

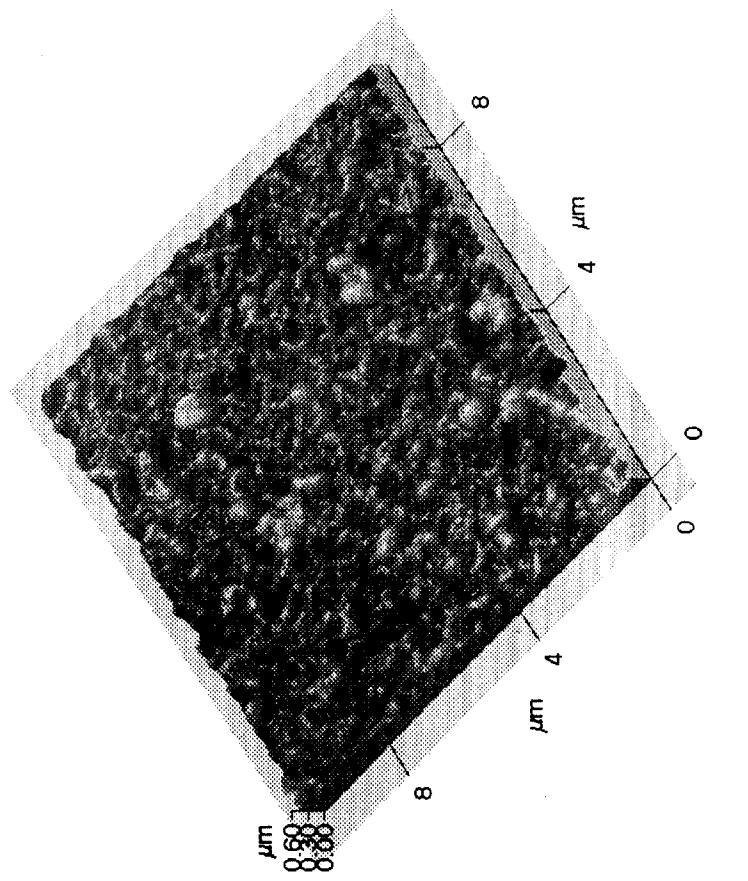
Typical Construction of Thin Film Composite Membranes



$t = \text{Approx. Total Thickness} = 175 \text{ microns} = 7 \text{ mils} * 1.0 \text{ mil} = 25.4 \text{ microns}$

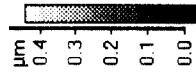
AFM

High Flux Membrane



25

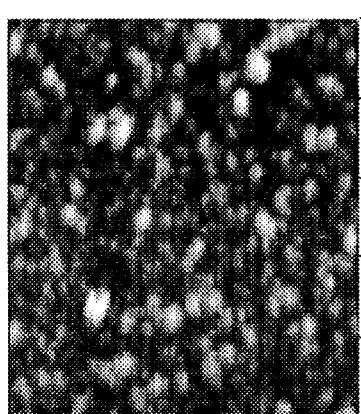
AFM



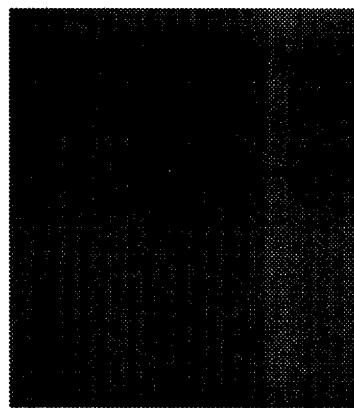
2T5

Area Statistics:

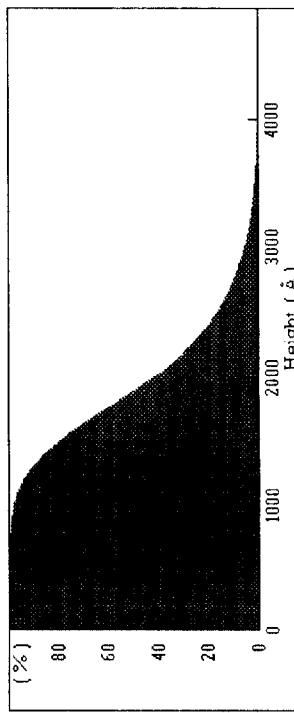
Peak to valley: 4879 Å
Rms rough: 578 Å
Ave rough: 447 Å



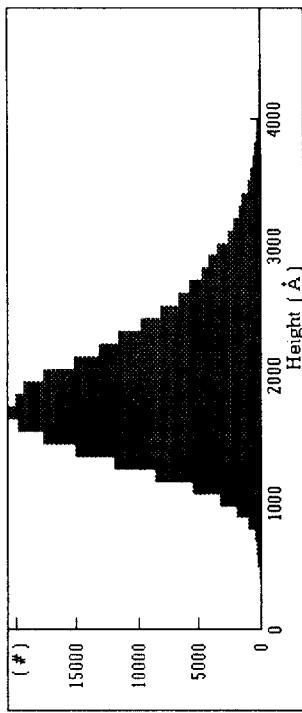
Selected Area



Bearing Ratio

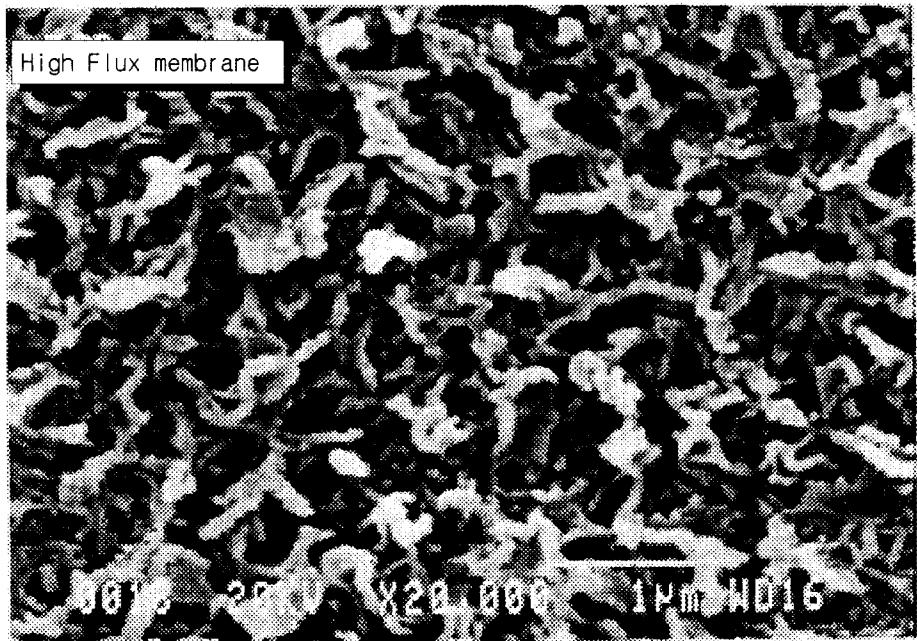


Histogram

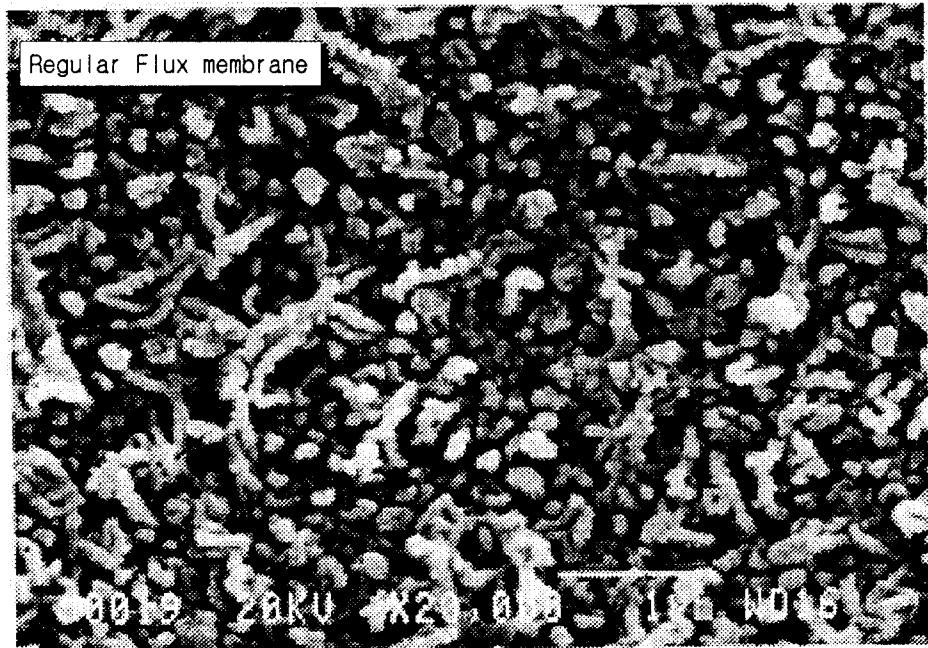


SEM

High
Flux
Membrane

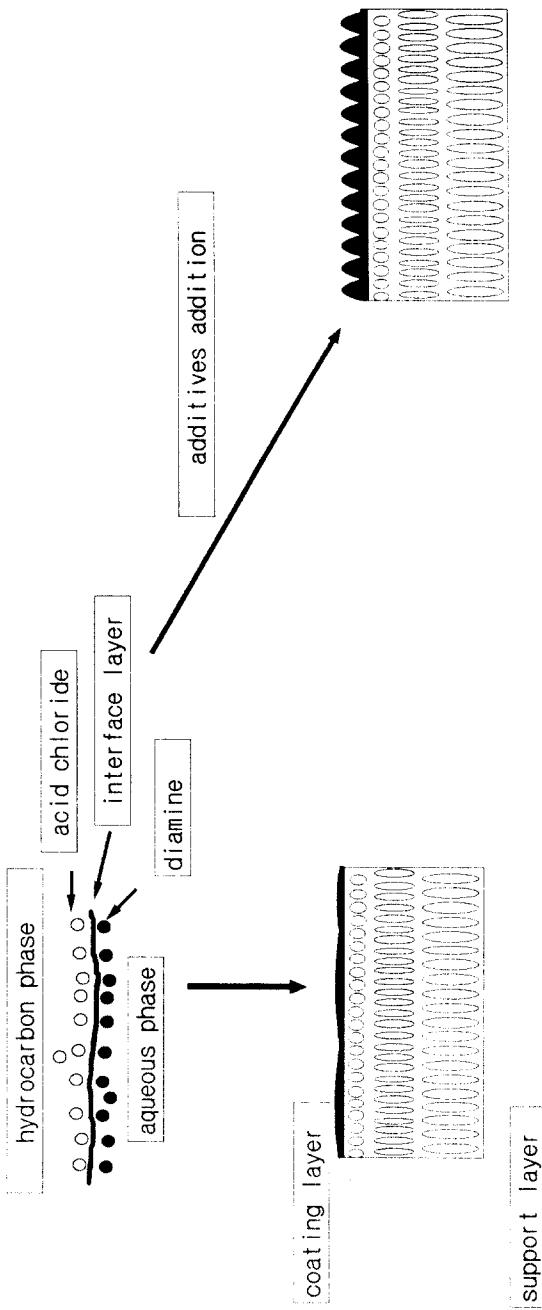


Regular
Flux
Membrane



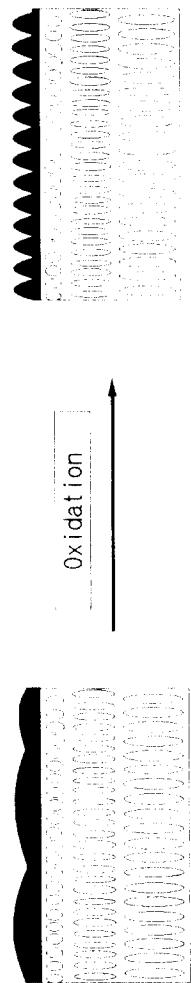
High flux concept

- 1) Inducing the Fluctuation in Interfacial Polymerization
: By add the chemicals in solutions



High flux concept

- 2) Etching the surface
 - : By using strong oxidative chemicals



High flux concept

- 3) Increasing the Pore size
: By using the Bulky monomer

