

# Preparation of Asymmetric PTFE Membranes and Their Application in Water Purification by Hyperfiltration

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## Synopsis

Asymmetric PTFE membranes suitable for purifying and separation by reverse osmosis also in aggressive conditions of the feed were prepared. A technique has been set up in order to obtain the necessary porous supports, using sintering of PTFE emulsions in the presence of salts. The pore distribution, hydraulic permeability, and shape by microscopic observation were investigated. Asymmetric membranes were then prepared by deposition of these porous supports onto dense thin PTFE films. Their properties were checked in a reverse osmosis plant with NaCl, saccharose, chromium, nickel, copper, detergents, and oil emulsions.

## INTRODUCTION

As previously reported,<sup>1-5</sup> the possibility has been verified of obtaining, via radiation grafting, PTFE membranes suitable for purification and desalination by reverse osmosis.

These membranes showed good performances, associated perhaps with their basic polymeric film structure.<sup>6</sup> The mean value for a 9- $\mu$ -thick (nominal) membrane was 90% rejection of sodium chloride with a permeability of about 100 l./m<sup>2</sup>d at 70 atm pressure. Such performance, even if interesting, is not unusual in comparison with the results obtained with other commercially available membranes.<sup>7-9</sup> However these membranes are endowed with exceptional chemical, physical, and biological stability, typical of the basic PTFE film, which would permit their use in very severe conditions of pH, temperature, and bacterial concentration. It would allow, in practice, a great saving in the management of plants operating, for example, hyperfiltration in purifying waste water or concentrating acid mining effluents or galvanic industries waste, by permitting a notable reduction in the plant running costs through less membrane replacement. It should be remembered, in fact, that in certain cases, as in whey concentration, recent estimates<sup>10</sup> indicate membrane replacement as 30% of the total cost.

It must also be remembered that the successful application of hyperfiltration depends, especially in the case of ecological problems, on the capacity that relatively small plants have to treat comparatively large daily volumes. From this point of view, the performances obtained by our membranes did not seem to us satisfactory, considering that the above-mentioned permeability values are obtained only with 9- $\mu$  membranes and thus creating handling difficulties.

It was preferred, therefore, to attempt to synthesize asymmetric films made from a high-selectivity thin layer supported by a porous layer of the same material, the purpose of which is to make the membrane resistant and manageable.

This paper will then deal with the preparation of asymmetric PTFE membranes and with the practical performances obtainable. Attention will be given to the setting up of the porous supports which themselves represent, in our opinion, a remarkable result, in relation to the application these films could have even in fields other than hyperfiltration.

## **PART I. POROUS SUPPORTS**

### **EXPERIMENTAL**

#### **Preparation of PTFE Films**

It has been verified by electron microscopy<sup>11</sup> that the structure of PTFE films obtainable by sintering from aqueous suspension<sup>12-14</sup> consists of dendritic fibrillar aggregates of the polymer particles present in the emulsion used.

In the same way it was established<sup>6</sup> that films obtained from emulsions composed of particles of different size or of different aggregation gave membranes with different physicochemical properties. On the basis of this observation, we were able to obtain highly permeable membranes exploiting sinterized films from special emulsions and with special techniques.

Unfortunately, the commercial PTFE films available are unable to give us such a variety of properties and we had to prepare them from aqueous PTFE suspensions kindly supplied by Montedison S.p.A.—Spinetta Marengo Plant.

In our research we have concerned ourselves with studying the best conditions both to obtain a thin, homogeneous film, without most of the defects one normally meets in commercial products, and to prepare porous films with different degrees of porosity.

#### **Preparation of Porous Films**

Porous PTFE films are commercially available under several trade names and for several uses and are obtained with different techniques.<sup>15-17</sup> None of these, as far as has been possible to ascertain, is made up from PTFE only, but all contain different minor components which, in our case, would have added to the obtained support a dimensional stability different from that of the real membrane and would have influenced the result of the radiation grafting process.<sup>5,18</sup>

Therefore, it was decided to induce a coagulation of the suspension so as to obtain, with subsequent sintering, a film with particles formed by aggregation

of numerous, much smaller particles (0.2–0.3  $\mu$ ) originally present in the suspension. According to this, the films so obtained should exhibit interspaces between one particle and the other, and thus exhibit "macropores." We had already verified, as mentioned above, that films obtained from suspensions of particles with different diameter showed different permeability characteristics.<sup>6</sup>

Since, however, the change in performance of the membranes obtainable from these films has not been found to be sufficiently wide, we thought that the presence of salts in the suspension would enable us to modify more substantially the performance of the films. The basis for this choice was the following: (1) the dissolved salts can influence the aggregation of the suspension; (2) during the film preparation, the water evaporates leaving salts crystals, and after removal of the salts by soaking, empty spaces remain in the film.

Salts were chosen on the basis of their solubility in the emulsion, their chemical stability, their melting point, and, above all, their crystal morphology. The last because the sintering requires a preliminary transition during which the suspension is spread out on a chromium-plated steel plate, and there, water is evaporated before the sintering or "baking."

As feedstock, a PTFE emulsion with these characteristics was employed: Trade name, Algoflon D 60. Composition, PTFE 16%; Triton X100<sup>3</sup> %; perfluoro-octanoic acid 0.3%; water to 100%. Particle size, 0.2–0.3  $\mu$ .

A large number of salts were examined, but in this study we will limit ourselves to describing the effect of three: NaCl, NaF, and BaCl<sub>2</sub>·2H<sub>2</sub>O.

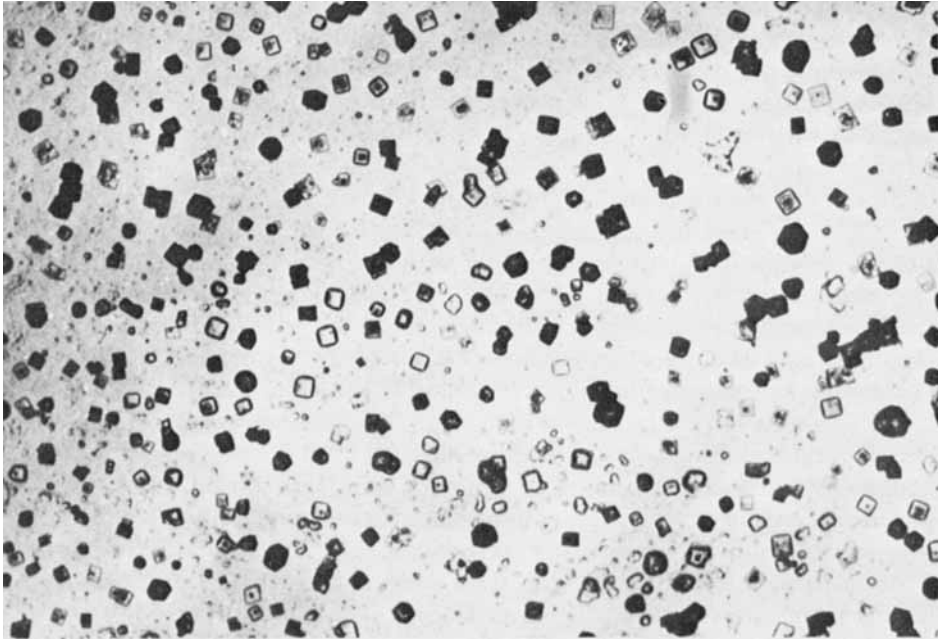
The properties of the three salts are given in Table I. In Figure 1 are reproduced the microphotographs of the crystals as they precipitate from the mother liquor of the suspension (mixture of water, Triton X100, and perfluoro-octanoic acid).

Since crystal size and particle aggregation rate are affected by temperature, we took care to check as carefully as possible the conditions of the preliminary drying process. This was achieved with a fan set to blow, tangentially to the surface of the emulsion, a jet of air at an adjustable temperature to bring about drying of the film in 10 sec. Likewise, the coating (at constant rate) and baking (sintering) conditions were controlled. The values of the essential parameters were as follows: Salt concentration, variable up to 30% (BaCl<sub>2</sub>) max conc. Coating rate, 0.004 m/sec. Drying temperature, 85–120 and 170°C. Sintering rate, 10 min. Sintering temperature, 400°C.

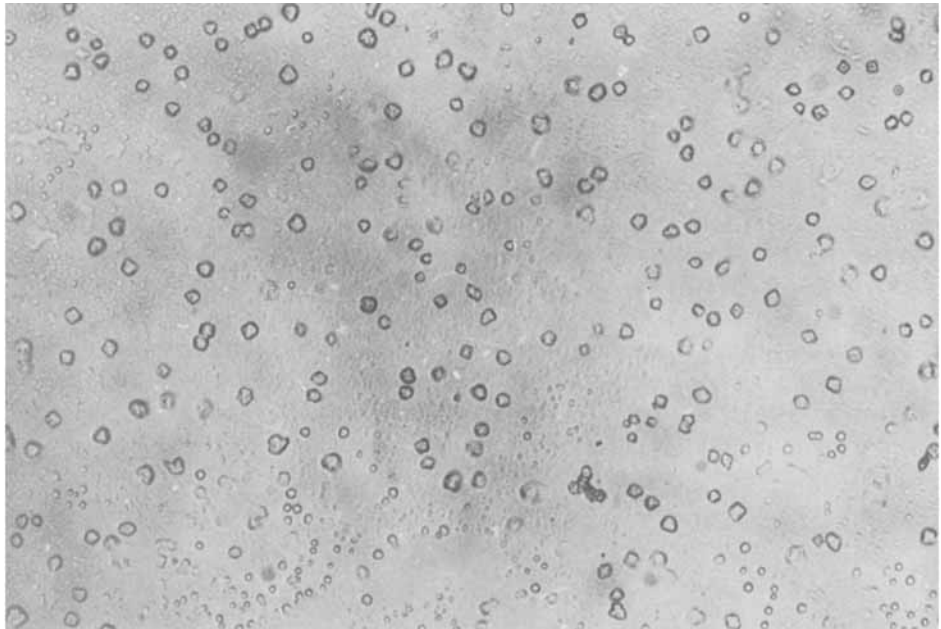
Immediately after sintering, the film was quenched in distilled water at 20°C. Then, another coating process was set up, and so on, up to the required thickness. The quenching process had the aim both to lock the polymer in a state of minimum crystallinity in order to obtain a higher rate of radiochemical grafting<sup>18</sup>

TABLE I Melting points and Water Solubilities of the Salts

Salt	Melting point, °C	Water solubility, g/100 cc
NaCl	801	35.7
NaF	988	4.22
BaCl <sub>2</sub> · 2H <sub>2</sub> O	962	58.7

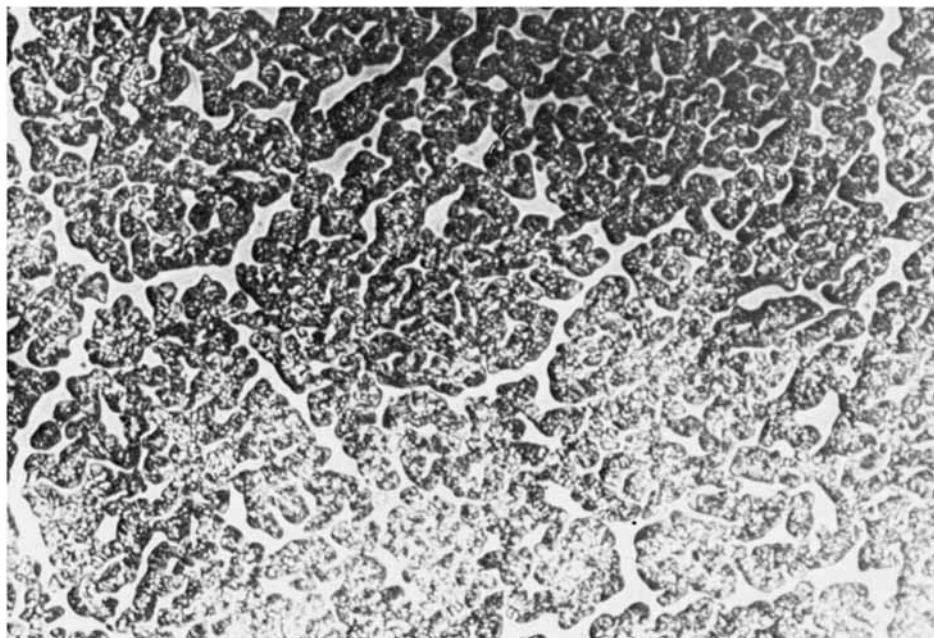


(a)



(b)

Fig. 1. Microphotograph of salt crystals as they precipitate from dispersant solution of the emulsion.



(c)

Fig. 1 (continued)

and to extract the salt from inside the pores.

After this treatment, in fact, the salt concentration that had reached 60 wt % in the dried film had a mean value of 3% (after just one water soaking).

As far as thickness is concerned, it was checked during the preparation with the number of successive layers of emulsion, but it was noted that according to the type and concentration of the salt, the final result varied as is shown in Figure 2(a) and 2(b).

This fact was taken into account in preparing films. The film was then removed from the plate, its thickness was measured followed by qualitative porosity control by a gas diffusion method, and transformed into a hydrophilic support by radiation grafting.

### Porosimetry and Microscope Observation

A very important aspect to evaluate the film performances is undoubtedly its porosity ratio or the pore diameters ratio of the porous film. For this purpose, a Carlo Erba porosity meter, Type AG 60, was used. A known amount (approx. 0.5 g) of cut porous film, carefully dried, was introduced into the dilatometer ampoule. The ampoule was then filled under vacuum with distilled mercury and assembled into the test circuit, which essentially is composed of an autoclave capable of reaching 1000 atm, connected to a mobile contact controlling the mercury level in the capillary bonded to the sample holder ampoule.

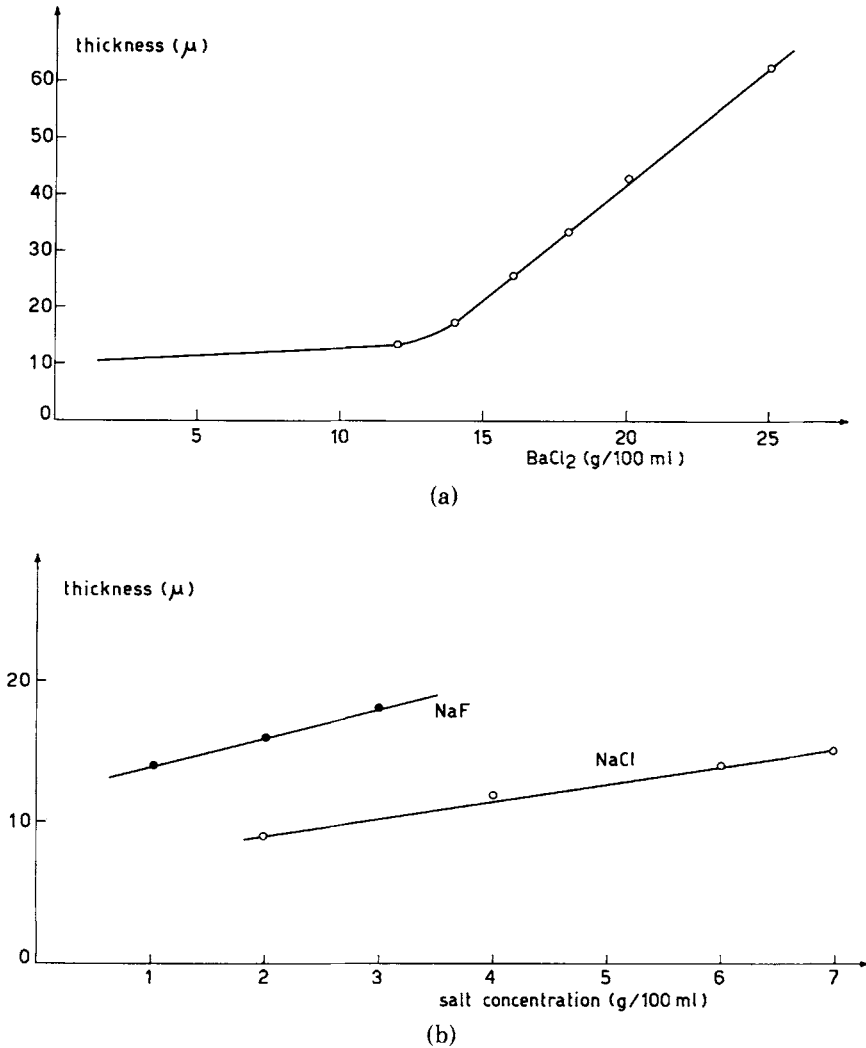


Fig. 2. (a) and (b) Film thickness vs salt concentration in the emulsion.

The movement of mercury as a result of the pressure is converted in terms of volume of filled pores, while the pressure at which this movement takes place is related to the mean pore diameter. It is, therefore, possible to measure varying pressures from 0 to 1000 atm and volume fractions in agreement with pore diameters from 75 to 75,000 Å. A blank is needed to give the volume decrease due both to mercury compressibility and to PTFE itself.

A high-resolution optical microscope was used for the observations on salt crystals on the surface and on film sections.

### Support Preparation

Earlier,<sup>1,2</sup> the high hydrophilicity of the membrane produced by our technique was pointed out. This hydrophilicity is coupled to a high possibility of dimen-

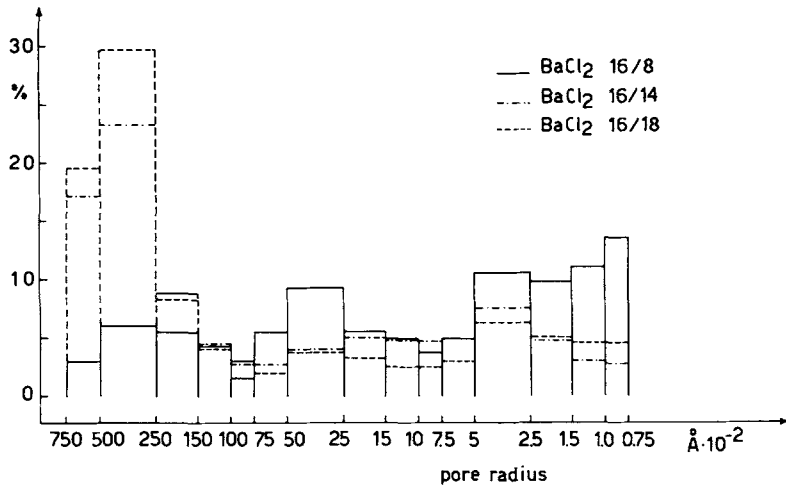


Fig. 3. Porosity ratio in films obtained from three different BaCl<sub>2</sub> concentrations.

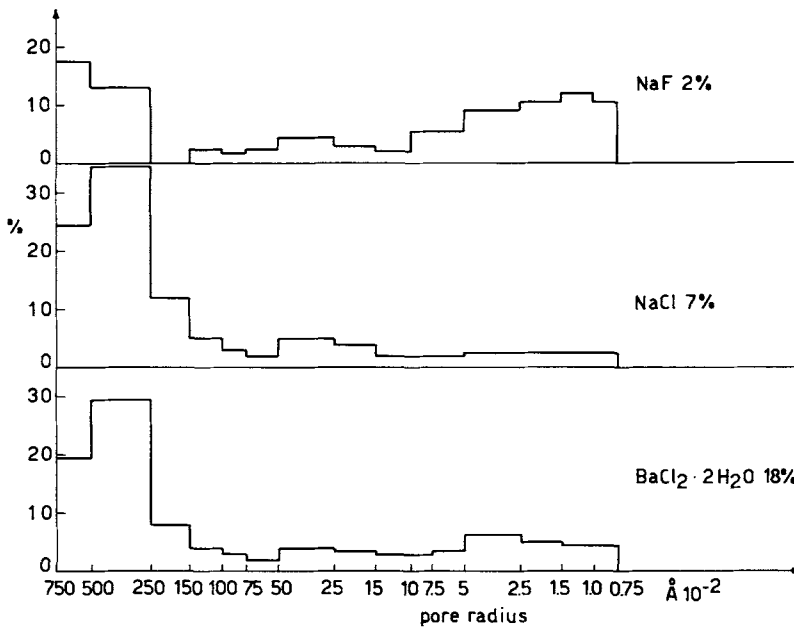


Fig. 4. Porosity ratio in films obtained from three different salts.

sional changes both depending on the moisture content and on the interaction which the ionic groups present in the membrane can have with the wetting brine. It follows that to have a suitable support for such a membrane, it must be able to follow membrane dimensional changes and show the same physicochemical properties; otherwise, creeping and incoherency between membrane and support can be expected.

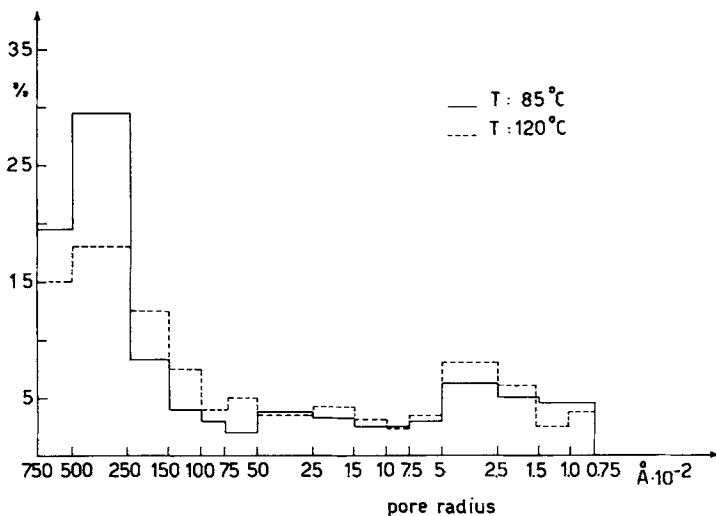


Fig. 5. Porosity ratio in films obtained from two different drying temperatures.

To overcome these difficulties, the porous film was subjected to the same grafting treatment necessary to transform the PTFE film into membranes. This treatment consists, briefly, of grafting styrene on PTFE by  $\gamma$ -radiation<sup>19</sup>. The amount of grafted styrene is expressed as % increment of the initial film weight. Grafted polymer can then be sulfonated to introduce ionic groups ( $\text{SO}_3^{2-}$ ). The supports have themselves some of the typical properties of the membranes (ion exchange), but obviously do not show permselectivity or semipermeability, nor do they repel dissolved substances during the reverse osmosis process. On the other hand, they present an average water permeability about three orders of magnitude higher than the membranes.

Tests carried out with these supports in our reverse osmosis laboratory plant<sup>3</sup> had, therefore, the aim to control the influence of different parameters on their permeability.

### Permeability Measurements

Permeability tests were carried out under these conditions: Test material, distilled water. Temperature, 25°C. Pressure, 30–70 atm. Water stream values through support, expressed in  $\text{l./m}^2\text{-day}$ , were taken at 0, 1, and 2 hr during the test. In some cases, the test was run up to 48 hr to study the support compaction, but, normally, the plotted stream values are always those taken at 1 hr.

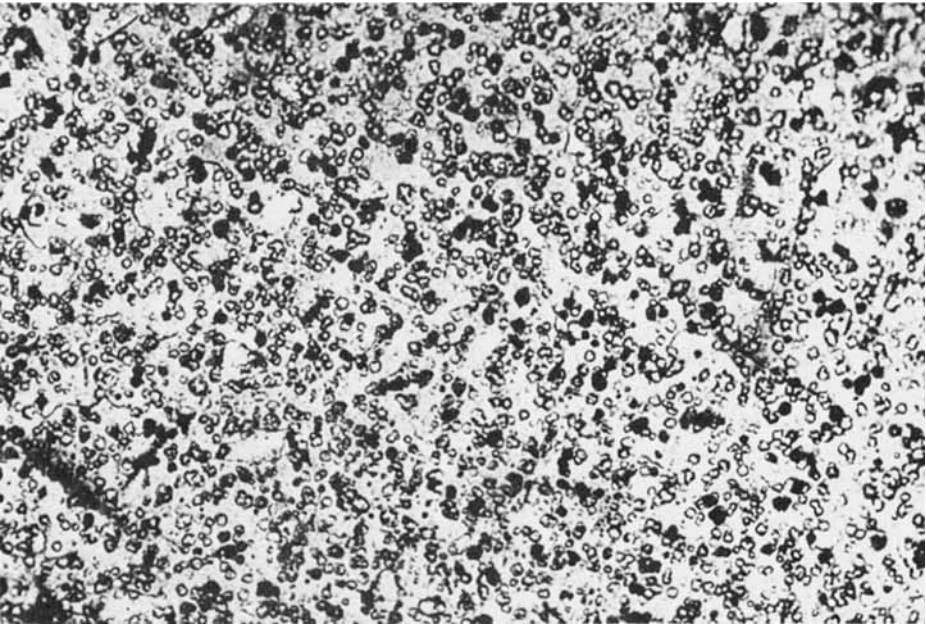
TABLE II Crystallizable Compounds Classification

Group	Specifications
A	Sublimation without decomposition
B	Sublimation and decomposition
C	Neither sublimation nor decomposition
D	No sublimation but decomposition



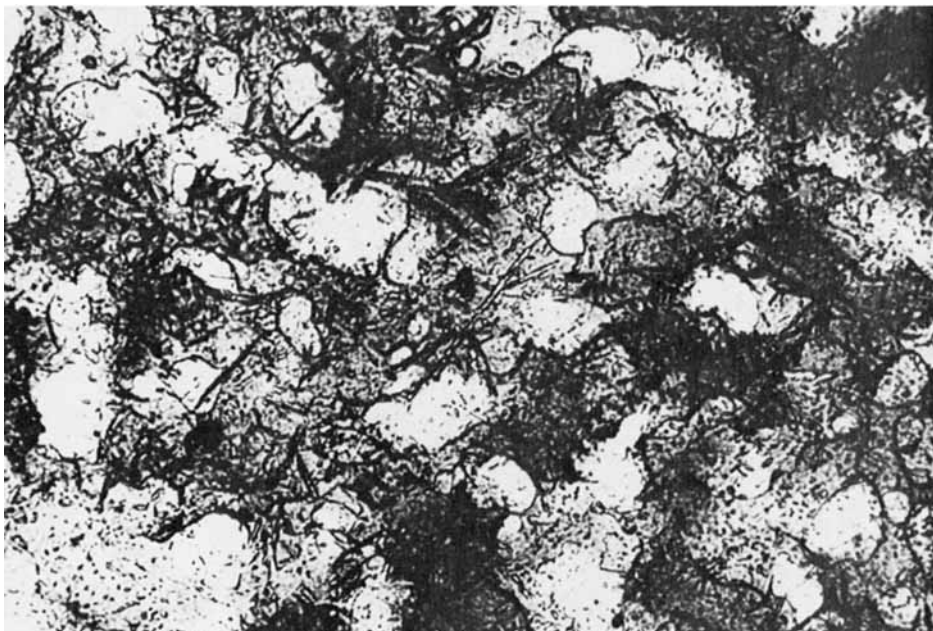


(a)



(b)

Fig. 6. Microphotographs of the surface of films obtained with three different salts.



(c)

Fig. 6 (continued)

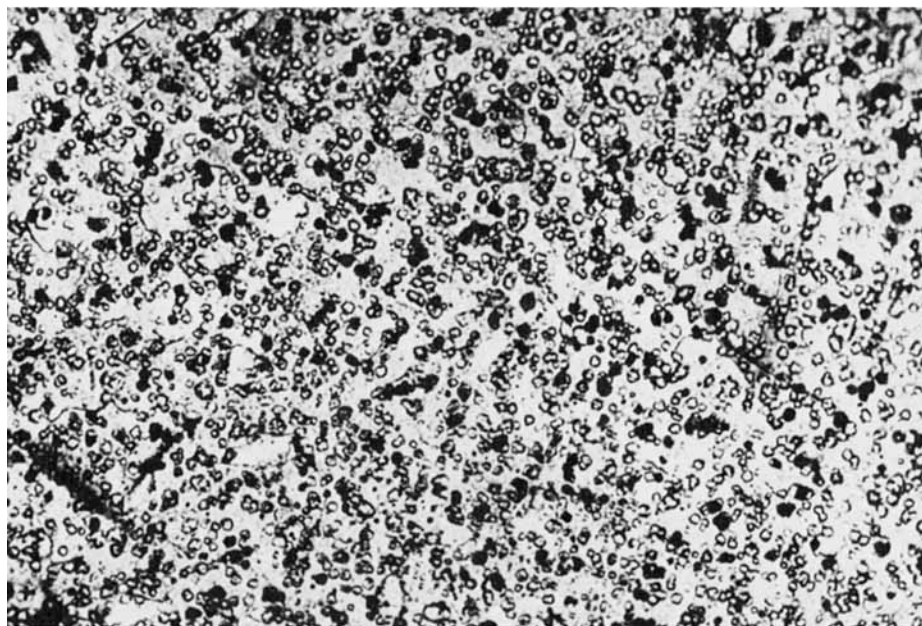
## RESULTS AND DISCUSSION

### Influence of Type and Concentration of the Salt and Drying Temperature on Pore Size

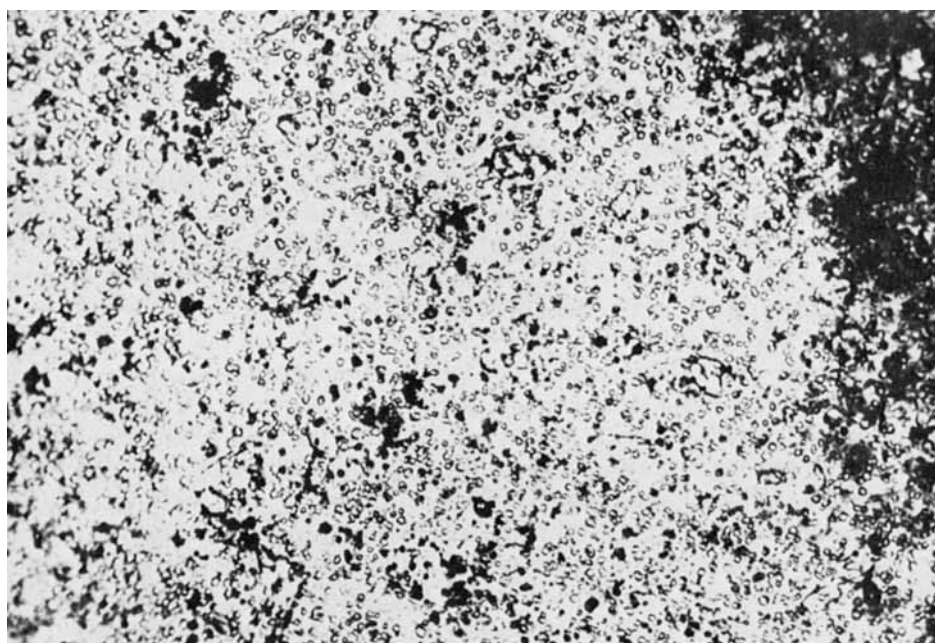
The prepared porous films were subjected to porosimetry, and the more representative results will be reported in the following figures.

Figures 3 and 4 present the influence of the salt concentration on pore size distribution. The last is influenced not only by the salt nature but also by its concentration. Further measurements done varying the film thickness did not show any relevant effect on the distribution, and an increase in film thickness apparently will decrease only the permeability. In order to control the effects of the crystallization rate and thus of the size of salt crystals and their influence on diameter and number of pores, some of the films were prepared and dried at different temperatures. These experiments we carried out using emulsions with  $\text{BaCl}_2$ , and the films obtained were subjected to porosimetry; results are reported in Figure 5.

It is important to remember that the preparation of the porous film was carried out with these leading criteria: (a) to control the coagulation of the emulsion with some agent operating in the liquid phase; (b) availability in the solid phase of some agent which would prevent the complete sintering of the particles. Moreover, these agents must not modify the chemical properties of the film and they should be easily removable.



(a)



(b)

Fig. 7. Microphotographs of the surface of films obtained from 2% NaF at different drying temperatures.

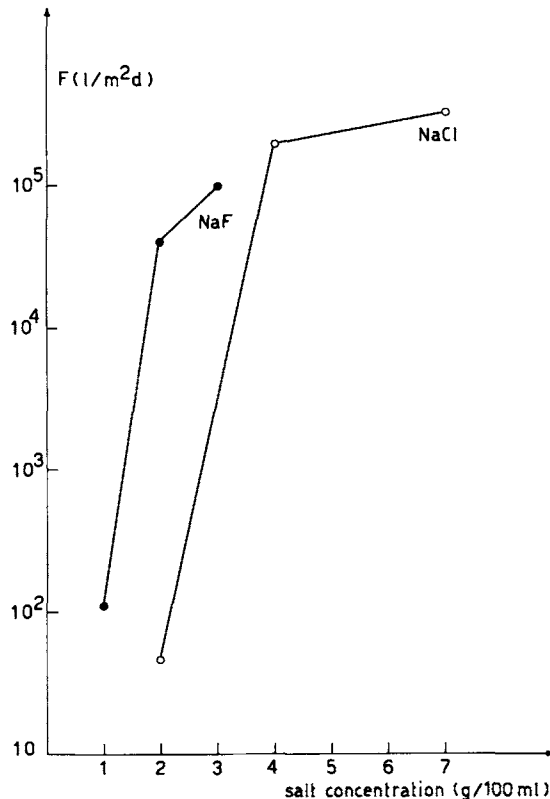


Fig. 8. Hydraulic permeability of the supports (at 30 atm) vs NaCl and NaF concentrations.

At the beginning, tests carried out with various typical coagulants gave only (HCl, acetone, etc.) defective films without appreciable and homogeneous porosity. The explanation for this behavior is based, in our opinion, on the high temperature needed for the sintering, which takes it to an initial melting with the possibility of occlusion of the eventual pores due to polymer softening. On the other hand, good results were obtained with compounds capable to be entrapped into the polymeric matrix.

Compounds able to form definite crystalline solids were used, divided into the groups shown in Table II, in connection with the operating conditions (high temperature) to which they had to be subjected during the film baking. Compounds of type A (i.e.,  $\text{NH}_4\text{Cl}$ ) and B (i.e., oxalic acid) did not give valuable results, while the best results were obtained with type C compounds (i.e., NaCl) and partially with type D (i.e.,  $\text{Ca}(\text{ClO}_4)_2$ ). The experiments previously reported were carried out on the basis of this classification. Moreover, the results of the microscope observation support as probable cause of pore formation the precipitation of crystals of solid particles stable up to  $400^\circ\text{C}$  in the polymer body, not neglecting the hypothesis of the suspension salting. Indirect evidence is given by the fact that some salts (certainly  $\text{BaCl}_2$ ) act as stabilizers of the suspension<sup>20</sup> because of the presence of a nonionic surfactant (Triton X100). Consequently, the pores in these films must have an average diameter similar to that of the crystals, and further evidence is given both from the comparison

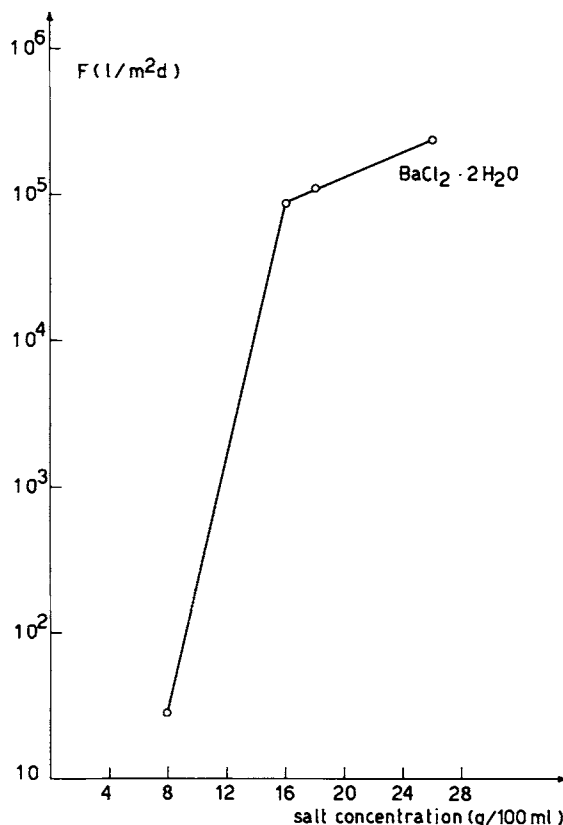


Fig. 9. Hydraulic permeability of the supports (at 30 atm) vs  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  concentration.

of the porosity ratio with diameter ratio of the crystals and from the microscope observations. Therefore, the experimental results can be explained as follows.

(a) **Effect of Salt Concentration.** The porosity ratios in Figure 3 show that an increase in salt concentration leads to an increase in large-diameter pores. This behavior can be explained keeping in mind the influence of salt concentration on the crystal growth; this leads, moreover, to a prediction of the existence of a certain concentration value at which the most crystalline structures will produce "closed cell" pores and then nonporous films. Permeability measurements will confirm this hypothesis.

(b) **Effect of Nature of Salt.** Differences among pore distributions obtainable with three different salts (Fig. 4) do not allow us to draw strictly quantitative relationships for the above-mentioned reasons, but allow us to draw the hypothesis that the pore "shape" is strictly related to that of the crystals. By "shape" we mean not only the crystal size, but even and above all its morphology, which, in the case of  $\text{BaCl}_2$ , has been considered above as the leading factor responsible for the unusual increase in porosity with film thickness.

(c) **Effect of Drying Temperature.** Comparison of the pore distributions (Fig. 5) shows that the number of thin pores increases as the temperature increases. As is well known, the crystal formation induced by rapid flashing off

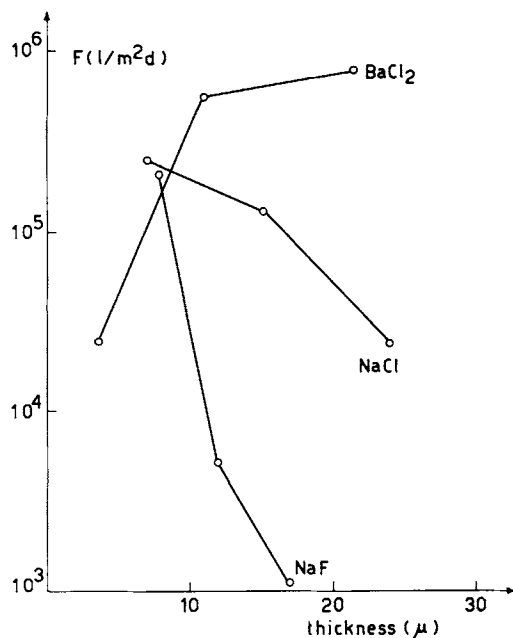


Fig. 10. Hydraulic permeability of the supports (at 30 atm) obtained from different salts vs thickness.

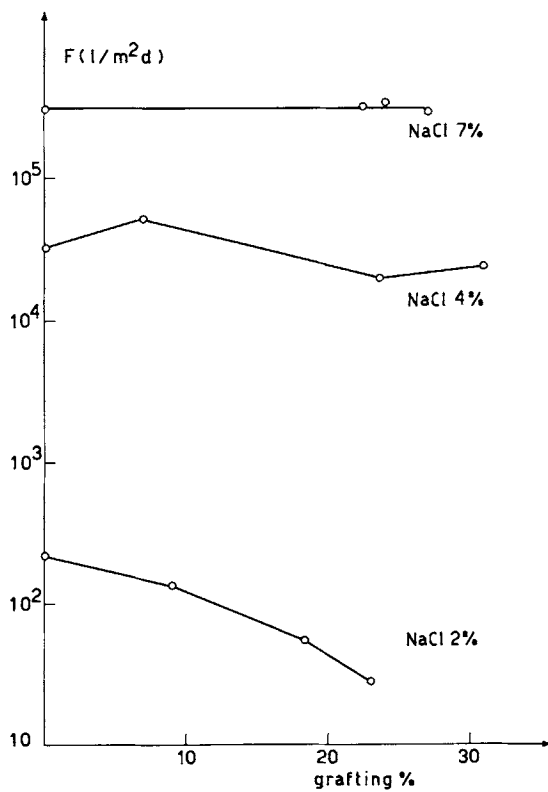


Fig. 11. Hydraulic permeability of the supports (at 30 atm) obtained from NaCl vs % graft.

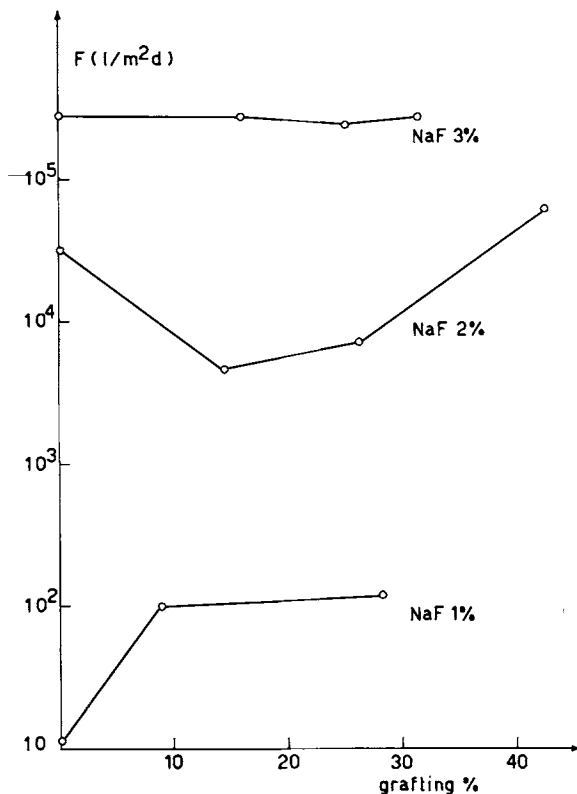


Fig. 12. Hydraulic permeability of the supports (at 30 atm) obtained from NaF vs % graft.

of the solvent generates small crystals and therefore produces pores with small diameters.

It must, nevertheless, be pointed out that if the solvent evaporates at an excessive rate, i.e., close to the boiling point, the pores are wider and more irregular (this result has been obtained in the case of  $BaCl_2$  emulsion dried at  $170^\circ C$ ); this is due to the mechanical effect of small vapor bubbles which prevent a regular deposition of the formed crystals.

It is also noteworthy that the salts are very easily extracted from the polymeric matrix, as has been confirmed by chemical tests.

### Microscope Investigation on Film Surfaces

Three films obtained from emulsions containing, respectively, NaCl, NaF, and  $BaCl_2$  were scanned by the optical microscope, and the microphotographs were compared with those of the isolated crystals (Fig. 1).

The surfaces appear different (Fig. 6) depending upon the salt employed and furthermore the particle aggregates partly resemble the morphology and the sizes of the salt crystals.

The microscope investigation has also clearly shown the influence of drying temperature on the pore size, as can be clearly seen by comparing the photos in Figure 7.

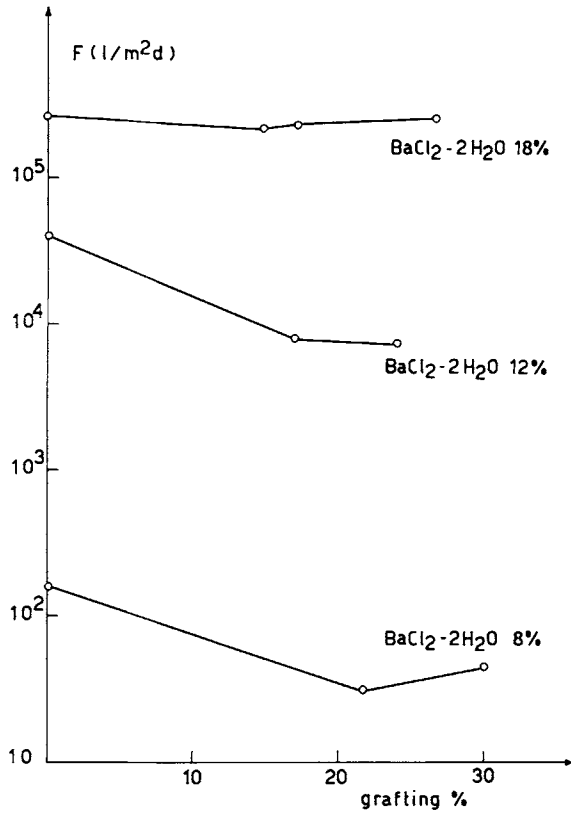


Fig. 13. Hydraulic permeability of the supports (at 30 atm) obtained from  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  vs graft.

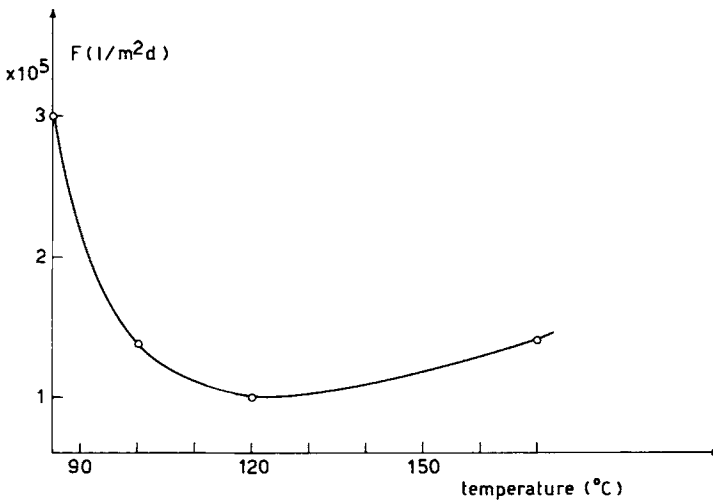


Fig. 14. Hydraulic permeability of the supports (at 30 atm) obtained from  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  vs drying temperature.



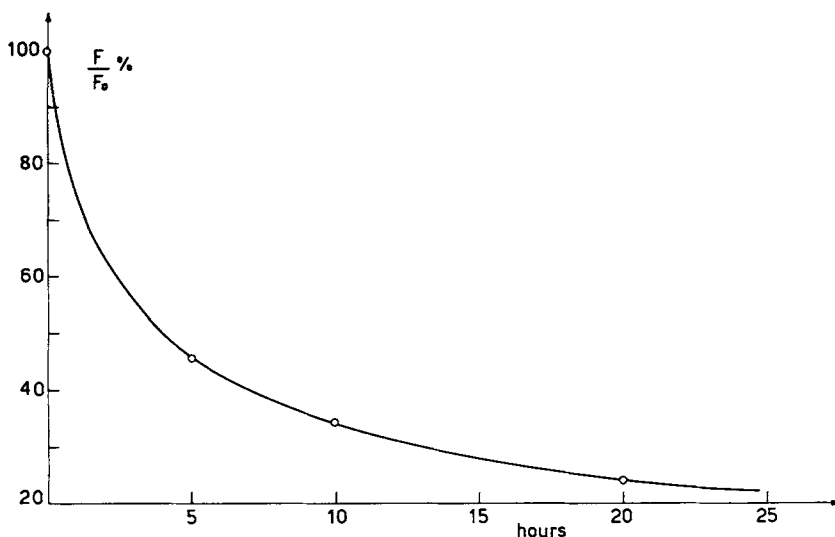


Fig. 15. Hydraulic permeability of the supports (at 30 atm) obtained from  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  vs testing time.

### Influence of Salt Concentration on Permeability

Figures 8 and 9 report the permeability versus NaCl, NaF, and  $\text{BaCl}_2$  concentration, respectively, in the initial emulsion, related to films with a thickness of 10 microns and 20% grafted styrene. The curves give a clear confirmation of the existence of a salt critical concentration below which a structure with open pores cannot exist.

### Influence of Thickness on Permeability

In Figure 10, permeabilities with NaCl, NaF, and  $\text{BaCl}_2$  are plotted versus support thickness. The values are related to supports prepared with constant salt concentrations in the emulsion and with a grafting of 20%.

We note that, in the case of NaCl and NaF, an increase in film thickness causes a sharp decrease in permeability, and this is obviously related to the pore size. As can be observed from the slope of the curves, this effect is higher for NaF, which produces very fine crystals, while for NaCl (larger crystals, Fig. 1) it is necessary to reach thicknesses three times larger in order to have the same permeability decrease.

In the case of  $\text{BaCl}_2$ , the permeability, instead of decreasing, increases with film thickness. This behavior can be related to the peculiar structure of pores derived from  $\text{BaCl}_2$  dendritic crystal precipitation. In our opinion, successive layers of emulsion cannot form a homogeneous film, owing both to deep irregularities in the substrate and to the thermal treatment necessary to "bake" the film.

### Influence of Styrene Grafting

In Figures 11–13 the values of hydraulic permeability at 30 atm of 10- $\mu$ -thick films obtained from three different concentrations of salt (NaCl, NaF, BaCl<sub>2</sub>) are reported.

The plotted curves can be interpreted if we analyze the change of the porous film structure after grafting and sulfonation. As reported elsewhere,<sup>18</sup> the styrene grafting begins at the PTFE surface; but for high yields (up to 30%), the inner body of the polymer is grafted and behaves like the polystyrene.

It follows that, because of the sulfonation of the grafted polymer, we are dealing with a film practically made from highly hydrophilic poly(styrenesulfonic acid) (PSSA). For low grafting yields, the hydrophilic groups are held in a stiff matrix and the cross section of the pores is controlled; if the grafting yield increases, the whole body collapses with a loss of the initial stiffness and an increase in permeability, as in the case of a wetted sheet of paper. For this reason the permeability passes through a minimum value increasing the grafting, as more clearly seen from Figure 11 (NaF).

This trend is less sensitive the higher the concentration of the salt added to the emulsion. The simplest explanation consists, in our opinion, of the fact that a higher concentration of dissolved salt can cause not only a higher number of crystals but also a higher number of large crystals and, therefore, of large pores. In these conditions (due easier diffusion of the monomer), the grafting, from the beginning, proceeds into the body of the film and induces a structure relaxation, and the permeability increases.

TABLE III R.O. Asymmetric Membranes Performances (NaCl 0.2 H)

Membrane no.	Thickness, microns	% Graft	Flux, l./m <sup>2</sup> · day	% Rejection
150	28	18.6	32	88
294	32	31	66	84
323	40	32	53	87
328	54	35	68	86
378	45	37	60	86
379	45	32	74	86
380	45	32	50	85
381	45	32	53	90
382	50	38	67	86

TABLE IV R.O. Asymmetric Membranes Performances (Saccharose 0.2%)

Membrane no.	Thickness, microns	% Graft	Flux, l./m <sup>2</sup> · day	% Rejection
292	32	30	70	99
293	32	32	80	80
294	32	31	58	99
323	40	32	53	90
327	51	36	62	95
329	23	37	85	90
331	30	33	67	95
332	30	31	55	90

### Influence of Drying Temperature

In Figure 14, permeability values are plotted versus drying temperature of the emulsion. The curve is referred to supports obtained with  $\text{BaCl}_2$  (this salt was normally used for the preparation of asymmetric membranes, but it is reasonable to extend the results to films obtained with other salts.

### Influence of Compaction

In Figure 15, the permeability versus testing time is plotted at 30 atm for a support obtained from 18%  $\text{BaCl}_2$ . This behavior, similar for all supports, is related both to the plastic properties of the PTFE film and to its spongy structure. Practically, the support, after 24 hr of testing, loses 80% of its permeability.

This fact does not influence its usefulness for the preparation of asymmetric membranes as the mean permeability of the supports is about  $10^5$  l./m<sup>2</sup>-day; the 20% of this value is enough not to interfere with the flow properties of the thin film.

## PART II. ASYMMETRIC MEMBRANES

### EXPERIMENTAL

#### Preparation of Asymmetric Membranes

The asymmetric membranes were obtained by deposition of porous layers on a 6–8  $\mu$ -compact, thin film previously prepared. The depositions of the porous layers were carried out without detaching the dense film from the plate. To obtain the support, emulsions containing  $\text{BaCl}_2$  (16% PTFE–18%  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) were employed, chosen on the basis of the previous porosimetry and permeability measurements.

The technique employed for the preparation of the porous support was exactly the same as described in part I: constant, too, were coating, baking, and quenching conditions. The only change, introduced on the basis of the results

TABLE V  
R.O. Asymmetric Membranes Performances (With Various Kind of Industrial Effluents)

Feed	Membrane no.	Thickness, microns	Flux, l./m <sup>2</sup> · day	% Rejection
2% $\text{NiSO}_4$	326	54	45	98
	327	54	40	94
$\text{CrO}_3$ 150 mg/l.	326	54	42	94
	327	54	40	97.5
0.5% Cu tartrate	326	54	60	99.4
	327	54	21	99.5
1% Oil emulsion	326	54	35	99.2
	327	54	26.5	99.9
Anionic detergents, 20 ppm	326	54	30	99
	327	54	35	97

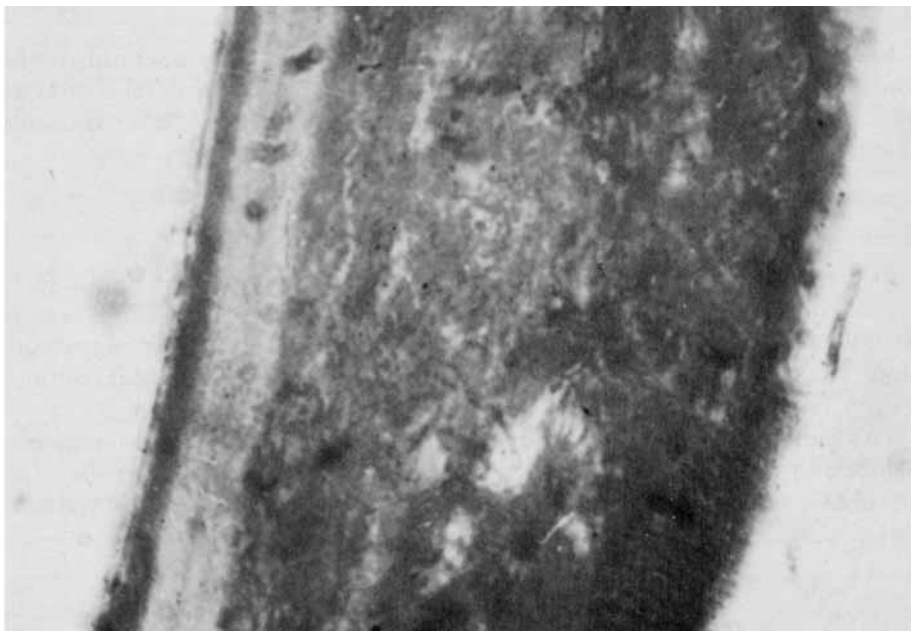


Fig. 16. Microphotograph of a section of asymmetric membrane.

obtained from experimental tests, was the drying temperature which was set up at 120°C to obtain a porous support more homogeneous and with small pore size.

The asymmetric film was easily detached from the plate; its thickness was measured (the thickness data reported in following tables are always referred to this stage of the membrane preparation). After a control of the absence of defects, the film was grafted with styrene and sulfonated, obtaining, in this way, the asymmetric membranes whose performances in reverse osmosis depend only on the thin layer of support. Performances were tested in the apparatus already used in the characterization of the porous films.

## RESULTS AND DISCUSSION

### Performances of the Membranes

All membranes, which differed only in the thickness of the porous layer, were subjected to reverse osmosis tests for the following purposes: (1) ascertain the asymmetric nature of the membrane; (2) ascertain the independence of membrane permeability from support thickness; and (3) verify the possibility to apply this type of membrane to the problems of industrial water desalination, concentration, and purification.

In Tables III and IV, the results obtained for 0.2M NaCl solution and saccharose (2 g/l.) are reported.

Some tests were carried out with industrial effluents; the results are reported in Table V.

The presence of a porous layer on the membranes so obtained appears not only from the microphotographic examination, as is shown in Figure 16, but also from the performances. If we compare the flux between these membranes and those prepared from a dense film and previously reported<sup>3</sup> for the same thickness, we obtain a ratio ranging from 6 to 8.

In spite of these good results, we were unable to obtain, using this technique, the main goal for which the study was undertaken. Indeed, at the beginning, we hoped to prepare membranes formed with very thin layers of dense film (say, 1–3  $\mu$ ) able to supply relatively high fluxes and easily manageable for added support.

Several experimental difficulties prevented us from being successful. The most important, in our opinion, are the following: (1) Under our experimental conditions, it was quite impossible to obtain homogeneous dense film of the required thickness (without defects). (2) Also, if the film is obtained, it does not bear up under the baking cycles necessary to prepare the support. (3) The crystals formed in the support may alter the thin layer.

## CONCLUSIONS

On the basis of the results obtained, we believe we have reached substantially two aims:

1. A new technique suitable to provide porous PTFE films which can be used not only as support for the thin membranes, but can be applied in other fields. A better control of the porosity is necessary, and it would involve a systematic study of the crystalline nucleation rate under the conditions which occur during the drying of the polymer suspensions.

2. New asymmetric PTFE membranes. This material, being not appreciably soluble in common solvents or chemical agents, on the one hand requires a relatively complicated preparative technique and, on the other, promises exceptional characteristics of stability and life.

It must be pointed out that, in spite of the heterogeneous nature of the matrix, the radiation grafting takes place homogeneously, at least under our experimental conditions, in spite of the different porosity of the membrane layers.

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Received September 1, 1976