

# Preparation of Reverse Osmosis Membranes by Surface Modification of Polymeric Films. I. Surface Acetylation of Cellulose

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## Synopsis

Surface acetylation of cellophane to afford an asymmetric membrane having high desalination ability (as high as 98% sodium chloride rejection) is described. The films were characterized by multiple-internal-reflectance microscopy (MIR), dyeing tests, light microscopy, and determination of water and sodium chloride transport properties in reverse osmosis cells. Surface modification employing acetyl chloride and acetic anhydride was studied in detail: the influence of the cellophane employed, the degree of cellophane activation, reaction time, reagent concentration, and diluent were assessed. Mixed acetylation reactions are also discussed as well as an evaluation of various postconditioning treatments used to increase desalination.

## INTRODUCTION

Much current interest is focused on the reverse osmosis separation process. To date cellulose acetate membranes are particularly successful in desalination by reverse osmosis. There are several methods of preparing membranes for reverse osmosis application, the most successful of which was developed by Loeb, Sourirajan, Manjikian, and others at the University of California at Los Angeles<sup>1,2</sup> It involves an asymmetric membrane characterized by a thin layer of cellulose acetate ( $0.25\mu$ ) formed by the evaporation of solvent, superimposed on a grossly porous section of cellulose acetate formed by the aqueous removal of the solvent and other water-soluble components. Other methods are casting into a porous support, casting a thin film and then transferring to a porous support, and hydroforming. Little attention, however, has been focused on creating a reverse osmosis membrane by surface chemical modification of a film already formed. The preparation of a carboxylic ion-exchange membrane by grafting poly(acrylic acid) onto cellophane and its hyperfiltration properties have been reported.<sup>3</sup> The present paper is the first of two describing the preparation of reverse osmosis membranes by surface modification of polymeric films.

Because of the utility of cellulose acetate as a reverse osmosis membrane, it was of value to initially study the cellulose-cellulose acetate system. Surface modification of regenerated uncoated cellulose film by acetylation was studied as

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a means to introduce salt discrimination. The objective of the research was to develop a new and versatile technique for obtaining ultrathin asymmetric reverse osmosis membranes.

Very little has been published on the acetylation of cellophane films. Although acetylation reactions have been widely studied, they were geared to the industrial production of modified cotton or cotton goods. The qualities that were sought were dyeability and increased resistance to microbial attack. Consequently, the exact experimental details of surface acetylation of cellophane films had to be defined in the laboratory.

### EXPERIMENTAL MATERIALS

Dry unplasticized cellophane used in the reported work (1 mil, 193-PUD-O gratis, E. I. DuPont de Nemours and Co.) was stored after its procurement in a constant-temperature (22–23°C) and constant-humidity room (45%) prior to use. Shipments of wet gel film (gratis, E. I. DuPont de Nemours and Co.) were obtained from the supplier packed in water and upon arrival were stored in 20% ethanol solution in a refrigerator.

The reverse osmosis properties of cellophane vary somewhat even when samples are taken from the same roll. Since flux and rejection properties can be measured with high precision, the difference in reproducibility observed must be related to nonuniformity in the samples obtained from the suppliers.

Reagent grade acid chlorides were used as received from the manufacturer without further purification. These included: acetyl (Allied Chemical Co.), isobutyryl (Matheson Coleman & Bell), malonyl (Pfaltz & Bauer, Inc.), and glutaryl (Pfaltz & Bauer, Inc.). Solvents, reagent grade, were dried over molecular sieves prior to use.

### Membrane Preparation

Acetylation of one side of the film was readily accomplished by means of conventional procedures, for example, (1) floating the cellophane on the surface of the acetylating medium (acetyl chloride or acetic anhydride in diluent) and (2) immersion of a sealed "envelope" of cellophane into the acetylation medium. After modification, the films were washed with water until neutral.

### Hyperfiltration Equipment

The equipment used in this study was similar to that described previously.<sup>3</sup> The desalination cells used for membrane evaluation were designed by Prof. McIntyre, University of Akron, and were obtained from the Premier Tool Co., Chicago. These cells are constructed entirely of stainless steel.

### Determination of Flux and Salt Rejection

The conditions employed for determination of the flux and salt-rejection properties summarized in this paper were: pressure, 1500 psi; pump rate, 62–64 cycles/min; water input, 11.4 cm<sup>3</sup>/sec; and sodium chloride concentration, approximately 10,000 ppm. The rejection values after 20 hr of testing were based on the final feed concentration. The values obtained for water flux and salt rejection are the average values of several runs, except when individual readings are given.

Water flux was calculated by collecting the effluent water in a measuring cylinder and determining the volume collected as a function of time.

The concentration of sodium chloride in both the starting brine solution and the effluent water were measured by the ion-concentration method of a type CDM2e Conductivity Meter (Radiometer-Copenhagen, Denmark: U.S. representative the London Company, Westlake, Ohio).

### Utilization of MIR Spectroscopy for Characterization of Acetylated Surfaces

Multiple-internal-reflectance infrared technique was established as a useful tool for assessing extent of surface acetylation of cellulose.

The infrared spectra of the surface-acetylated membranes were obtained with a Perkin Elmer 137 spectrophotometer. The MIR infrared technique employed a model 12 dual-beam internal-reflection attachment manufactured by Wilks Scientific Corporation, South Norwalk, Connecticut. Two 45° KRS-5 internal-reflector plates (52.5 × 20 × 2 mm) were employed as prisms. Spectra of films having a degree of substitution (D.S.) from 0.93 to 2.88 were obtained from authentic samples by employing the model 12 reflectance attachment. Powdered cellulose acetate samples (Tennessee Eastman, X-9814-88-1 to -7; D.S., 0.93-2.88) were prepared for MIR analysis by pressing them into sheet form with a press.

The relationship between degree of substitution and relative band intensities of the 5.68- $\mu$  carbonyl band and the 8.15- $\mu$  ester band was determined by using the 9.5- $\mu$  acetal-ether band as an internal standard. The 9.55- $\mu$  band is common to both components and did not change appreciably as the composition varied. Optical density (*D*) ratios of the acetal-ether band found at 9.55 $\mu$  and the 5.68- $\mu$  carbonyl and the 8.15- $\mu$  ester bands were used to obtain calibration curves. The calibration curves are not straight lines but are analogous to those reported for the quantitative estimation of the extent of acetylation by employing the potassium bromide disc technique.<sup>4</sup> Correction of the three absorption bands by a common baseline, arbitrarily assigned as the transmission value recorded at 5 $\mu$ , did not change the curves appreciably.

## RESULTS AND DISCUSSION

### Pretreatment

The extent of acetylation was studied at various levels of activation. It is well known that cellulose acetate can be prepared in a shorter time and more uniformly if the cellulose is swollen before acetylation. Various organic liquids such as alcohols, as well as water, increase the acetylation rate. In this study the cellulose was water activated prior to reaction with acetyl chloride/benzene (1:2 by volume).

Cellophane (193-PUD-O) was activated prior to treatment by equilibration at relative humidity (R.H.) ranging from 45 to 100%. Reaction times were also varied. These variations had a pronounced effect on the reactivity of the cellophane. Films containing the greatest amount of absorbed water (100% R.H.) were the most reactive, as demonstrated by the highest salt rejection reached (91.9%) and lowest reaction time (7.5 min) (Fig. 1). The salt rejection increased as the reaction progressed, reached a maximum, and then began to decrease.

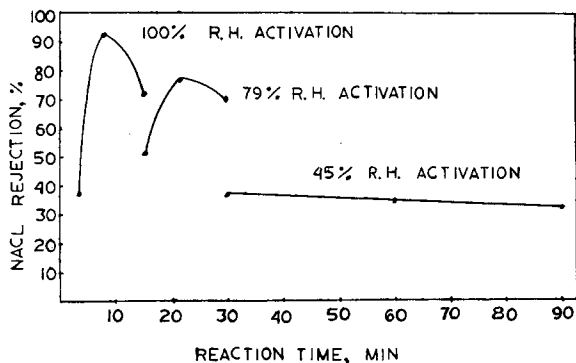


Fig. 1. Effect of reaction time and degree of activation on NaCl rejection.

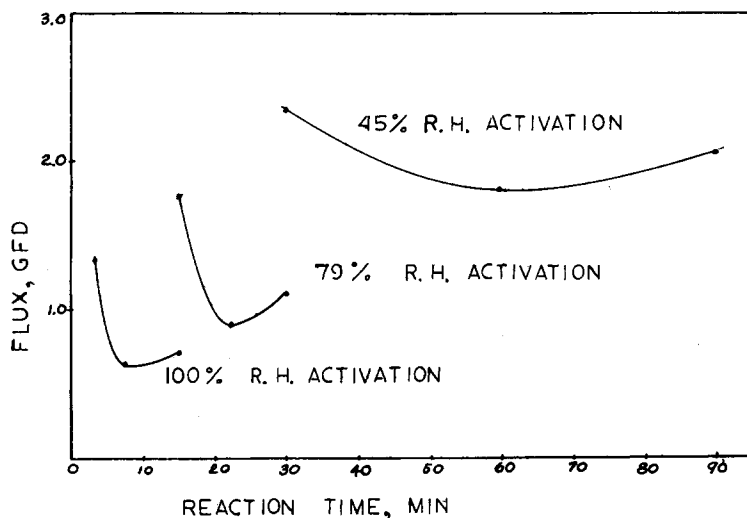


Fig. 2. Effect of reaction time and degree of activation on flux.

The degree of substitution of the surface layer was higher after 15 min of reaction than after 7.5 min (1.73 vs. 1.47). The D.S. of the cellulose acetate is important in reaching higher salt rejections. However, the reaction medium can act to swell the modified film. Acetyl chloride is also a swelling agent while benzene is a diluent to limit swelling. The effect of diluent on the reaction is very complex. The reaction medium appears to affect the cellulose acetate structure after it is formed. The cellulose acetate layer can be swelled and then removed after it is formed. Hence, although higher D.S. is achieved with longer reaction time, the layer is porous as is evidenced by increasing flux after the dense layer (flux minimum) is formed (Fig. 2).

During testing, the salt rejection increases as a function of time, which can be attributed to the effect of pressure. Pressure causes compaction of the cellulose acetate structure and excludes much of the water. As a result of the compaction, intermolecular distances are decreased, more crosslinks are formed, and desalination improves. It is notable that the membranes do not suffer appreciable flux decline with time at high pressures as compared to the Loeb membranes.

Activation of the cellophane with formamide was studied and compared. The extent of acetylation was negligible for the nonactivated and the formamide-treated cellophane as indicated by MIR spectroscopy. The membranes displayed only small increases in salt-rejection properties in formamide-activated membranes. This study indicates that water is more effective in opening the structure of cellulose than a polar liquid such as formamide.

### **Porous Cellophanes**

The preparation of selective membranes with higher flux than obtained previously was sought by acetylating a more porous cellophane. Since dried wet gel has a flux more than twice as high as the 193-PUD-O studied previously, it was a suitable substrate for initial investigations. DuPont wet gel was dried, activated, and acetylated with acetyl chloride in benzene (1:2) in a similar manner. The test results showed the more porous substrate does indeed afford a membrane with higher flux (0.82 vs. 0.62 gfd and 20 hr) without sacrificing selectivity (91.6 vs. 91.9%).

The effect of reaction time on the reverse osmosis properties of more porous cellophanes acetylated with acetyl chloride in benzene (1:2) was also studied. As was observed previously the salt rejection increased as the reaction progressed; it reached a maximum and then began to decrease. The D.S. of the surface layer was higher after the 15-min than the 7.5-min reaction (1.65 vs. 0.75 D.S.). After the 22.5-min reaction the film delaminated. This was observed in other surface-modified films when a very thick acetate layer was formed. Delamination was attributed to the topochemical nature of the reaction and to structural differences in the thickness direction. In addition, it was observed that the reaction medium affects the cellulose acetate structure after it is formed.

### **Surface Layer**

#### *Layering Effect*

When a very thick acetate layer was formed, the film could be peeled apart in layers. These membranes had very low salt rejection (i.e., 18.5%). The formation of layers of cellulose acetate is not unexpected. The reaction is probably topochemical as in esterification with acetic anhydride; that is, the reaction advances from layer to layer through the film.

#### *Membrane Directionality*

The surface-acetylated films displayed membrane directionality. The films showed greater desalination and lower flux when the acetylated surface was placed toward the brine (0.63 gfd and 83.5% vs. 4.2 gfd and 16%). As also occurs in the Loeb membranes,<sup>5</sup> the dense acetate layer provides essentially all the resistance to water and salt flux.

#### *Depth of Modification*

The depth of surface modification of cellophane acetylated with acetyl chloride was studied by dye sorption tests in conjunction with a light microscope. Many different combinations of direct cotton dyes that do not stain acetate with contrasting acetate dyes that do not stain cotton would be suitable for determining qualitatively the uniformity of acetylation within a sample. However, for fol-

lowing acetylations more closely by the aid of a microscope, a particular violet, Pontamine Fast Heliotrope B (DuPont), is used.<sup>6</sup>

The films were dyed in a manner similar to that reported previously.<sup>6</sup> The acetylated films were treated with the direct-dyeing Pontamine Fast Heliotrope B (DuPont), which dyes cellulose violet without staining acetate, and with Acetamine Yellow RR (DuPont), which dyes acetylated cellulose but does not stain cellulose that is unacetylated.

The products were dyes in a bath containing 1% Pontamine Fast Heliotrope B and 4% Acetamine Yellow RR calculated on the weight of the film. The dyeings were washed well with cold water and dried. Then the films were cold-mounted in Plexiglas and epoxy resin for examination of the cross sections by optical microscopy. After the mold was set, the samples were ground and polished.

Dye sorption tests in conjunction with light microscopy are often employed in the cotton industry to follow the extent and quality of acetylation.<sup>6-8</sup> This technique was found useful for determining the uniformity of acetylation, but it was not successful in assessing the degree of surface modification.

#### *The Reaction Medium*

The effect of diluents on acetylation rate has often been noted in the literature. Workers<sup>9</sup> reported that the acetylation of cellulose in the fiber state with 1 part  $\text{Ac}_2\text{O}$  and 3 parts organic diluent with 1% (based on linters) of  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$  proceeded faster with  $\text{CCl}_4$  ( $\text{CCl}_4 > \text{ethers} > \text{ketone solvents}$ ).

The acetylation of activated 193-PUD-O cellophane employing acetyl chloride was studied as a function of diluent. The reverse osmosis properties of the films are summarized in Table I. The observed results can be attributed to the effect of diluent on the formation of cellulose acetate. The D.S. of the cellulose acetate is important in reaching higher salt rejections. For benzene, carbon tetrachloride, and petroleum ether diluents, D.S. values of 1.47, 1.35, and 1.29, and respective salt rejections of 91.9, 88.5, and 49.8% were obtained.

There are two possible explanations for this phenomenon and both may actually contribute. One involves the breaking of H bonds in the cellulose by the more polar solvent mixture. The other is based on the postulate that the reaction of acetyl chloride is an  $\text{S}_{\text{N}}2$  reaction and is increased in rate by an increase in the polarity of the medium. A comparison of dielectric constants shows that the results can be attributed to both explanations.

TABLE I  
Effect of Diluent on Acetylation<sup>a</sup>

Diluent	Flux, gfd	NaCl Rejection, %
Benzene	0.62	91.9
Petroleum ether	1.29	49.8
Carbon tetrachloride	0.48	88.5

<sup>a</sup> Activated 193-PUD cellophane (100% R.H.) was acetylated for 7.5 min at 25°C with acetyl chloride in a diluent (1:2 volumetric ratio), quenched with water, washed until neutral, then tested. The reverse osmosis properties were determined after 20 hr of test time.

TABLE II  
Effect of Quenching Solvents<sup>a</sup>

Reaction time, min	Quench	Quench time, min	Flux, gfd		Rejection, %	
			1-3 hr	>20 hr	1-3 hr	>20 hr
7.5	H <sub>2</sub> O	10	0.67	0.62	76.4	91.9
7.5	H $\emptyset$	5	0.31	0.29	47.0	92.6
	H <sub>2</sub> O	5				
5	MeOH	5	1.55	1.31	32.2	54.1
	H <sub>2</sub> O	5				
5	H <sub>2</sub> O	10	0.78	0.62	63.2	92.2

<sup>a</sup> Activated 193-PUD cellophane was acetylated with acetyl chloride in benzene (1:2 volumetric ratio) at various reaction times as indicated at room temperature.

The reaction carried out in a nonswelling medium is influenced by the diffusion rate of the reagent into the cellulose film. A more polar diluent promotes penetration or diffusion of the mixed reagent into the internal spaces of cellulose fibers and makes the acetylation smooth and homogeneous.

The effect of reaction time on the reverse osmosis properties of cellophanes acetylated in carbon tetrachloride and in petroleum ether was also studied. As was observed in studies in which benzene was employed as the diluent, the salt rejection increased as the reaction progressed; it reached a maximum and then began to decrease. In the acetylation reaction employing carbon tetrachloride, the D.S. of the surface layer was higher after the 10- and 15-min reactions than after the 7.5-min reaction (1.97 and 2.0 vs. 1.35). The reaction medium appears to affect the cellulose acetate structure after it is formed.

When petroleum ether is employed as the diluent, the reaction is slow and the highest salt rejection occurs after 15 min of reaction time. It would be expected that longer reaction times would afford the same results as in the cases of carbon tetrachloride or benzene. The longer reaction time (15 min) with carbon tetrachloride afforded a very porous and thick layer of cellulose acetate.

#### *Quenching Solvents*

The medium employed for quenching the acetylation reaction may be considered as a postconditioning treatment. Benzene and methanol were used to quench the acetylation reaction of activated 193-PUD-O with acetyl chloride in benzene (1:2). As can be seen from the data in Table II, in comparison to a water quench, quenching the film in methanol results in greater water and salt permeability, whereas quenching in benzene affords a much tighter membrane.

#### *Acetylation Employing Acetic Anhydride*

Acetic anhydride in 2,2'-dichlorodiethyl ether with perchloric acid catalysts was reported to afford a D.S. of 2 in 5 min.<sup>10</sup> During the program the acetylation reaction employing acetic anhydride on the cellophane surface was thoroughly studied. Activated 193-PUD-O was reacted under a wide variety of reaction conditions. The effect of degree of activation, reaction time, catalyst concentration, aging, and stirring on the reaction were carefully assessed. The results are summarized in Table III.

TABLE III  
Acetylation Employing Acetic Anhydride, Acetic Acid, and Perchloric Acid

Concentration <sup>a</sup>	Variation	Flux, gfd	Rejection, %
40/12/18/0.3	Age 45 min <sup>b</sup>	0.16	98.0
80/24/36/0.5	Do not age <sup>b</sup>	1.37	35.3
80/24/36/2.0	Age 1 hr <sup>b</sup>	1.15	44.9
80/24/36/0.5	Age 45 min <sup>b</sup>	0.37	90.1
	Water activate <sup>c</sup>		
80/24/36/1.0	Age 45 min <sup>b</sup>	0.16	82.0
	Water activate <sup>c</sup>		

<sup>a</sup> 193-PUD-O cellophane (activated at 100% R.H.) was reacted in the listed ratio of milliliters of 2,2'-dichlorodiethyl ether/acetic anhydride/acetic acid/perchloric acid.

<sup>b</sup> The acetylating solution was allowed to stand for the indicated time prior to use.

<sup>c</sup> Activated by brushing with water.

After the addition of perchloric acid, it was noticed that the acetylating mixture became gradually darker, became black, and then became lighter. The time factor to reach the deepest color qualitatively appeared to be 45–60 min. In Table III the results of some typical experiments show the effect of solution aging. Solutions that were not allowed to age and were used immediately after mixing did not afford a membrane as highly salt rejecting as that formed when the solutions were aged for 45 min (35.3 vs. 98% rejection). Apparently aging enhances the process of chain organization into denser structures.

The perchloric acid concentration is critical. Excess acid results in a membrane with lower desalination properties (44.9 vs. 98%). This is probably due to cellulose degradation occurring at the higher concentration of acid.

Some typical tests showing the effect of pretreatment are also summarized in Table III. Activation at 100% R.H. afforded the most highly salt-rejecting membrane (98%). Activation by brushing with water afforded a cellophane so reactive that it nearly dissolved during the reaction.

The level of acetylation appears to be reached rapidly; increasing reaction times did not appreciably further the extent of acetylation after 30 min. Stirring was not found to affect reaction rate or the homogeneity of the layer. The homogeneity of the cellulose acetate layer was determined by the uniformity of swelling prior to reaction.

#### *Mixed Esters and Ethers*

Recently, it was reported that a highly selective membrane for saline water conversions was prepared from cellulose acetate-butyrate.<sup>11</sup> Hence mixed-surface acetylation of cellophane was also studied.

Activated 193-PUD cellophane was allowed to react with various ratios of butyryl chloride and acetyl chloride in benzene. Since the optimum conditions for acetylation of this cellophane with acetyl chloride are 7.5 min at 25°C, these conditions were employed in the mixed acylation reactions. The films were characterized for extent of acylation by MIR.

Films that were surface modified with butyryl chloride and various ratios of butyryl chloride and acetyl chloride did not display adequate desalination properties. The infrared spectra of the modified surfaces indicate that acylation occurs only to a slight extent with butyryl chloride alone (0.2 D.S.) and to a



limited extent with the various ratios of acetyl chloride/butyryl chloride in benzene (4:2:8, 3:1:8, and 2:2:8 afforded 1.5, 1.1, and 1.1 D.S., respectively).

Since the acetylating medium affects the cellulose acetate structure after it is formed and the polarity of the diluent affects the extent of acetylation, it is likely that because of its low reactivity (it afforded only a D.S. of 0.2 when employed alone) butyryl chloride acts as a polar diluent affecting both the structure of the modified layer and the reaction rate. Apparently in the acylation-butyration reaction, the acetylation rate is faster than the butyration and the extent of acetylation tends to become lower as the acetyl/butyryl ratio is decreased.

Acetylation studies were also extended to cellophanes that were surface modified to contain methoxy methyl ether groups. The ether groups would be expected to impart greater stability to the acetate structure. 193-PUD-O cellophane (stored at 45% R.H. and 25°C) was surface modified with chloromethyl methyl ether in benzene (1:1) for 30 min at 25°C. It was then activated at 100% R.H. and allowed to react with acetyl chloride in benzene (1:2) for 7.5 min at 25°C. The reaction afforded a very thick modified layer. However, the film was brittle and could not be tested.

Next, acetylation employing acetic anhydride, acetic acid, and perchloric acid catalyst in 2,2'-dichlorodiethyl ether was assessed. The data showed that a film of mixed acetate-methoxy methyl ether is highly salt rejecting with no sacrifice in flux as compared to a pure acetate layer (90.0% and 0.65 gfd vs. 91.9% and 0.62 gfd).

#### *Postconditioning Treatments*

In attempts to increase salt rejection, various acetylated cellophanes were annealed in a water bath at 70°C for 1 hr. Heat treatment resulted in anomalous behavior. In some cases the effect of heat treatment was to reduce the flux and increase the salt rejection. However, in other cases annealing increased the flux and decreased salt rejection. It was also found that heat treatment of 38°C for 30 min had a deleterious effect. The results strongly indicate that annealing swells the substrate (the flux increases from 0.51 to 0.66 gfd). Consequently, salt rejection is reduced from 96.0 to 86.2%.

The use of pressure as a morphology-modifying technique was also studied. Salt rejection increases as a function of testing time and can be attributed to the effect of pressure. It is likely that the pressure employed during testing (1500 psi) serves to densify the acetylated layer. Pressure would cause compaction of the cellulose acetate structure and excludes much of the water. As a result of the densification, intermolecular distances are decreased, more hydrogen-bonded cross-links are formed, and desalination improves. Hence, prepressurizing the modified film may serve as a postconditioning treatment to improve salt rejection.

Prepressurizing films of varying degrees of acetylation is indeed beneficial. Pressurizing the film increases salt rejection at no expense of flux. However, pressurizing is more beneficial in films of lower degree of acetylation than in films of higher degree of acetylation (62.7% rejection increased to 72.8% vs. 92.8% increased to 94.4%).

Time is an important factor. Films pressurized for longer periods of time (30 min) display decreased desalination ability. Again, temperature has a deleterious effect. Films pressurized for 10 min at 50°C have lower desalination

properties than the control (61.1 vs. 65.7%). It is likely that higher temperatures and increased time cause the film to dry out and, hence, poor reverse osmosis properties are observed.

The effect of formamide treatment on the acetylated surfaces was also studied. The acetylated surface was dipped in formamide, exposed to the atmosphere for 5 min, then immersed in water. This treatment did not affect the extent of acetylation, as indicated by infrared studies of the films. Generally, regelling the acetate layer increased flux and decreased salt rejection (e.g., 1.10 gfd, and 68% vs. 2.7 gfd and 21.8% after treatment). However, if the acetate layer contained imperfections as indicated by low salt rejection, formamide treatment was beneficial (e.g., 3.2 gfd, and 11% vs. 2.3 gfd and 32% after treatment).

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### References

1. S. Loeb and S. Sourirajan, UCLA Engineering Report 60-60 (1960); *Advan. Chem.*, **38**, 117 (1963).
2. S. Manjikian, S. Loeb, and J. McCutchan, "Improvement in Fabrication Techniques for Reverse Osmosis Desalination Membranes," paper presented at 1st International Symposium on Water Desalination, Washington, D.C., Oct. 1969.
3. W. H. Baldwin, D. L. Holcomb, and J. S. Johnson, *J. Polym. Sci. A*, **3**, 833 (1965).
4. R. T. O'Connor, E. F. DuPre, and E. McCall, *Textile Res. J.*, **28**, 542 (1958).
5. J. R. Toppers, V. Harrison, and J. Johnson, Jr., *J. Appl. Polym. Sci.*, **10**, 969 (1966).
6. C. F. Goldwait, E. Buras, Jr., and A. S. Cooper, *Textile Res. J.*, **21**, 831 (1951).
7. E. M. Buras, Jr., A. S. Cooper, E. J. Keating, and C. F. Goldwait, *Am. Dyestuff Rept.*, **43**, 203 (1954).
8. A. S. Cooper, S. T. Voorheis, Jr., E. M. Buras, Jr., and C. F. Goldwait, *Textile Ind.*, **116** (1), 97 (1952).
9. K. Thinius, W. Thuemmler, and P. Schmidt, *Plast. Kautschuks*, **12**(3), 161 (1968).
10. E. Dyer and H. D. Williams, *Tappi*, **404**, 14 (1957).
11. Department of the Interior, Office of Saline Water, News Release, March 17, 1969.

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