

## ***Long-Term Permeation of Water through Neoprene***

Measurement of the permeation of liquids and gases through organic polymers is well characterized. The usual procedure is to establish a steady state permeation over a period of several days or a few weeks. The permeability of the membrane is then calculated and assumed to be a constant value over a long exposure time.<sup>1</sup> For simple polymers, where no change such as backbone or sidegroup degradation can occur, this is a valid assumption. However, where exposure can cause a change in the polymer or perhaps change the composition of additives, such a short-term determination may be questionable.

Three questions then arise in connection with using rubber as a water barrier for a very long time. (1) Is the permeation rate constant over a very long period? (2) What is the condition of the permeant as it emerges from the membrane; i.e., does it transport soluble components of the rubber? (3) What is the effect on the rubber? The answers to these questions are especially pertinent to the problem of protecting electrical systems designed for long lifetime.<sup>2,3</sup>

### **EXPERIMENTAL**

Discs of Neoprene G (Joy Manufacturing Co., proprietary formulation) were cut from cured sheets of 25-mm (0.10-in.) thickness. These were mounted in standard permeability cups (Gardner-Park Permeability Cups, Ref. ASTM D 1653-72<sup>4</sup>) into which had been placed either deionized (DI) water or 3.5% sodium chloride solution (simulated seawater). The cups were then placed in a desiccator over calcium sulfate, and the whole assembly was kept in an oven at 60°C. The cups were weighed once a week and water (weight) loss vs. time was plotted. Permeation rate was calculated based on an area of 25 cm<sup>2</sup>.

To determine the presence of soluble salts on the outside of the rubber, the face was washed with DI water of conductivity  $5 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ . Conductivity of the wash water was then measured again to observe any increase that occurred.

### **RESULTS AND DISCUSSION**

Four samples were used, two with saltwater and two with deionized (DI) water. One set of DI and saltwater tests was run for 316 days and the other set for 201 days, both at 60°C.

Figure 1 shows the data for the longer experiment and illustrates clearly that salt water permeates the Neoprene G at a constant rate (linear weight loss) while DI water permeates at an increasing rate (curvilinear weight loss).

Table I summarizes the data from both sets of samples. Rates of saltwater permeation are in good agreement. Both initial and final rates are given for DI water permeation. The long-term sample showed a nominal 40% increase in rate over 316 days while the shorter-term experiment showed only an 8% increase. The shorter experiment was begun 115 days after the first one to allow the rubber samples to age at room temperature. Neoprene undergoes further crosslinking during such aging, especially, as in this case, when the material is freshly molded. This further curing results in a lower permeability. Because of the higher solubility and permeation of DI water over salt water, the DI water data would be more sensitive to changes in degree of crosslinking than would the salt water data.

There are several possible explanations for this nonequilibrium behavior. The composition of the Neoprene may change by leaching of components into the liquid permeant, thereby opening pores to increase the capillary flow component of water transport (as opposed to activated diffusion). Changes in composition of the elastomer and the residual permeant are discussed below.

Another reason for the continually increasing fresh-water permeation may be the solubility of DI water in this Neoprene formulation, due, of course, to the additives. Other studies of this phenomenon at 5°C, 25°C, and 50°C over 24–40-day terms have shown that fresh water continues to be absorbed by Neoprene (WRT) without reaching equilibrium.<sup>5</sup> Because permeability is dependent on solubility, a continual increase in the latter will affect the former similarly.

Finally, a variation on the preceding explanations may be used. Absorption of water in elastomers which contain water soluble fillers has been shown to create pockets of solutions which continue to

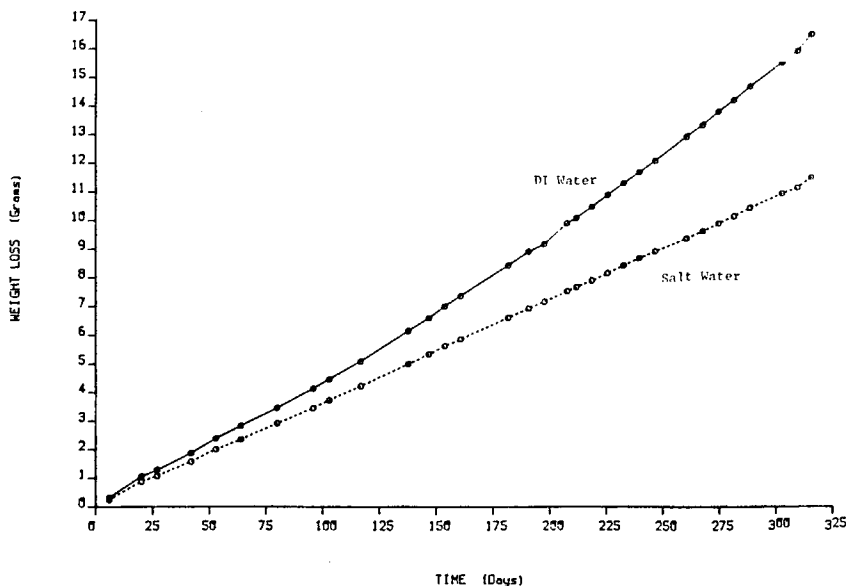


Fig. 1. Permeation of deionized water and 3.5 wt % NaCl solution (salt water) through neoprene G at 60°C.

grow until the osmotic pressure is balanced by the pressure exerted by the rubber containment.<sup>5-9</sup> This phenomenon introduces a very complex picture for water permeation: there are pockets of permeant; mechanical stresses are induced in the rubber matrix; and channels may be created for water diffusion.

The outer (dry) faces of the permeated rubber samples were washed with DI water to determine if soluble salts were present. Conductivity data in Table I show only very slight changes.

The internal water permeant was changed by the long-term aging. The water was pale yellow. Elemental analysis by emission spectroscopy showed a notable change in four of the 16 metals which were monitored (Table II).

Aluminum appeared in the salt water at a concentration 700 × that in fresh water. Inspection of the permeation cell revealed internal corrosion worse in salt water than in fresh water, hence the source of aluminum. Sodium, of course, originated from the Neoprene; and salt water removed much less than did fresh water.<sup>5</sup> The source of magnesium and iron was also the Neoprene.

The permeated rubber was also analyzed for metals by emission spectroscopy. Of the 16 metals present, only sodium showed any appreciable change. Salt water reduced the sodium content of the rubber by 17% (from 0.12% to 0.10%) and DI water reduced it by 92% (to 0.01%).

TABLE I  
Long-Term Permeation Results

	Total time (days)	Total water permeated (g)	Conductivity of face wash <sup>a</sup> ( $\Omega^{-1} \cdot \text{cm}^{-1}$ )	Permeation rate <sup>b</sup> ( $\text{mg}/\text{cm}^2 \cdot \text{day}$ )
1st Set				
DI	316	16.53	$8.6 \times 10^{-6}$	1.69/2.35
Salt	316	11.51	$7.6 \times 10^{-6}$	1.43
2nd Set				
DI	201	8.10	$6.6 \times 10^{-6}$	1.51/1.63
Salt	201	7.47	$11.1 \times 10^{-6}$	1.44

<sup>a</sup> Pure DI water is about  $5 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ .

<sup>b</sup> For DI water initial and final rates are given.

TABLE II  
Analysis of Residual Permeant

Metal	Deionized water (%)	Salt water (%)
Al	$7 \times 10^{-5}$	$5 \times 10^{-2}$
Mg	0.18	0.05
Na	0.01	1.9*
Fe	$7 \times 10^{-4}$	$3 \times 10^{-3}$

\* Corresponds to 4.8% NaCl solution.

### CONCLUSIONS

Although 3.5% salt water behaves as expected during permeation through Neoprene and establishes a steady state permeation rate, deionized water does not. Rather, DI water shows an ever increasing permeation rate, even after 316 days at 60°C.

Salt from salt water or ionic components of the rubber do not seem to diffuse through with the water flux.

DI water leaches most of the sodium from Neoprene and has a high solubility. The resulting swollen, more porous membrane may be the reason for the higher permeability observed for DI water over salt water.

Recent long-term permeation experiments have been run at 25°C on WRT, GRT, and TRT Neoprenes, all with compositions similar to one another.<sup>10</sup> After 1800 h only the WRT Neoprene showed a large increase in permeability.

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PATRICK E. CASSIDY  
GARY C. ROLLS

Texas Research Institute, Inc.  
Austin, Texas 78746

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