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THE EFFECT OF SEAWATER ON POLYMERS. (U)

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The Effect of Seawater on Polymers

LEVEL II

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November 14, 1979

NAVAL RESEARCH LABORATORY
Washington, D.C.

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Transducer Fluids	Environmental Tests
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	Diffusion

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The extent of interaction between a fluid and a polymer is monitored by changes in weight, dimension, and hardness. Results of the measurements reported here show that the type of interactions are dependent upon the specific material. Some materials undergo a simple diffusion process, while others interact in a complex manner, with several processes occurring simultaneously. Those materials that exhibit complex behavior require further study with appropriate end-use tests.

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CONTENTS

EFFECT OF SEAWATER ON POLYMERS

BACKGROUND

Elastomers and plastics used in sonar transducers and other marine applications are often in direct contact with seawater. A problem with this interaction was found when the DT-513 sonar transducer's mounting bracket failed. The Naval Sea Systems Command (NAVSEA 63X-T) determined that the cause of failure was due to corrosion by seawater. The Naval Weapons Support Center suggested using a plastic mounting bracket, but a final decision was made to use a cupric-nickel alloy because of its proven long-term compatibility in transducers. However, use of this alloy is very expensive. As part of the Sonar Transducer Reliability Improvement Program (STRIP), the Underwater Sound Reference Detachment (USRD) of the Naval Research Laboratory undertook the study of seawater interactions on elastomers and plastics. Study of the interactions between a polymeric material and seawater has been limited to examination of changes in physical properties of materials after their submersion in the ocean for many years. Results of a study of this type by Bell Laboratories were reported by Connolly *et al.* [1] in 1970.

There are many ways to monitor the extent of interaction between a fluid and a polymer. One frequently used indicator is the change in weight of a polymer after immersion in a fluid. This is a practical indicator since both a loss in weight (dissolution of the polymer of an additive) and a gain in weight (migration of water molecules and/or salt ions into the polymer matrix) indicate degradation of elastomeric properties. Additional indicators, previously used in similar studies, include changes in dimension and hardness. A loss or gain in thickness is caused by processes similar to those responsible for a loss or gain in weight. An increase in hardness is due to either a leaching of plasticizer or, at elevated temperatures, further curing of the elastomer. A decrease in hardness is caused by absorption of water (or seawater), which acts as a plasticizer. Experimental techniques are presented in Appendix A. Since these indicators do not simulate an end-use test, additional testing is needed to get a realistic prediction of the effects on elastomers exposed to seawater under natural operational conditions.

A diffusion process obeys Fick's First Law of diffusion. A discussion of the thermodynamics and mathematics of diffusion may be found in any standard physics text (e.g., Ref. [2]).

If the fractional weight change of the polymer is used to monitor the extent of diffusion, then according to Fick's First Law

$$\frac{dm}{dt} = -DA' \frac{dc}{dx}. \qquad (1)$$

In Eq. (1) $\frac{dm}{dt}$ is the mass of water per unit time diffusing normally through an area A' with a concentration gradient of $\frac{dc}{dx}$. D is the diffusivity that is assumed to be constant under isothermal conditions. The mass dm of water diffusing into the polymer is related to the distance dx by a constant that is dependent upon the concentration gradient; therefore,

$$dm = K\,dx. \tag{2}$$

Substitution yields

$$\frac{dm}{dt} = -DA'K\,\frac{dc}{dm}. \tag{3}$$

In experimental practice, small changes are observed rather than exact differentials, so Eq. (3) becomes

$$\frac{\Delta m}{\Delta t} = -DA'K\,\frac{\Delta c}{\Delta m} \tag{4}$$

or

$$\Delta m^2 = -DA'K\,\Delta c\,\Delta t. \tag{5}$$

Dividing by m_o^2 gives

$$\left(\frac{\Delta m}{m_o}\right)^2 = \frac{-DA'K\,\Delta c\,\Delta t}{m_o^2}. \tag{6}$$

If $t_o = 0$, then $\Delta t = t - t_o = t$. Then Eq. (6) becomes

$$\left(\frac{\Delta m}{m_o}\right)^2 = k\,t \tag{7}$$

where $k \equiv \frac{-DA'K\,\Delta c}{m_o^2}$.

Equation (7) can be rewritten as

$$2\log\left(\frac{\Delta m}{m_o}\right) = \log t + \log k \tag{8}$$

or

$$\log\left(\frac{\Delta m}{m_o}\right) = \tfrac{1}{2}\log t + \tfrac{1}{2}\log k. \tag{9}$$

As seen in Eq. (9) a log-log plot of the fractional weight change versus time will have a slope of 0.5. A value for k can be found by extrapolating the plot back in time to one hour (t = 1). A log-log plot that is not a straight line or has a slope other than 0.5 indicates that several processes are occurring simultaneously.

The constant k is related to the absolute Temperature T by the Arrhenius equation

$$k = A \exp(-E_a/RT) \tag{10}$$

or

$$\ln k = (-E_a/RT) + \ln A \tag{11}$$

where A is a statistical factor, E_a is the energy of activation for the process, and R is the gas law constant. It is evident from Eq. (11) that a graph of the natural logarithm of k as a function of 1/T will yield a straight line with a slope of $(-E_a/R)$ and an intercept of ln A. A relationship between fractional weight change, time of exposure, and temperature is produced by combining Eq. (10) with Eq. (7) to yield

$$\left(\frac{\Delta m}{m_o}\right)^2 = A\, t \exp(-E_a/RT). \tag{12}$$

From this equation a prediction can be made about the lifetime of a component under normal conditions. The values of A and E_a can be derived from experiments where elevated temperatures are used to accelerate the process of degradation.

This report is a preliminary study of the degradation of polymers exposed to water and artificial seawater. Several aspects of water-polymer interactions are of interest. First, a comparison of the effect of water as opposed to the effect of seawater will be drawn. Second, for polymers that undergo a diffusion-controlled process, a calculation of the energies of activation and statistical factors will be made. Finally, predictions will be made about the lifetimes of the polymers under normal conditions.

EXPERIMENTAL RESULTS

A detailed description of the behavior of a variety of acoustic-grade elastomers upon extended immersion in water and seawater is obtained by observing graphs of weight, dimensional, and hardness changes versus time of exposure. These graphs are presented in Appendix B.

All of the elastomers finished the study without severe degradation, with the exception of polyurethane (PRC 1538) and natural rubber.

Table 1: Materials Studied

GENERIC TYPE	FORMULATION	REMARKS
Polychloroprene	Neoprene W	Cured by a manganese oxide-zinc oxide catalyst.
Polychloroprene	Neoprene 5112	Cured by a lead oxide catalyst.
Chlorobutyl	H862A	-
Butyl	B252	-
Silicone rubber	V121	-
Polyurethane	PRC 1538	-
Natural rubber	BFG 35007	-
Polycarbonate	Lexan	-
Epoxide	EPON VI	-
Nylon	-	-

Polyurethane (PRC 1538) immersed in either fresh or seawater at 60 and 80°C disintegrated after 1300 hours. The disintegration is probably due more to the elevated temperature than to exposure to fresh water or seawater. This conclusion was drawn from the fact that the samples at 10 and 25°C showed no signs of degradation even though they achieved the same fractional weight change as did the samples that disintegrated. Natural rubber immersed in fresh water at 80°C underwent a drastic deformation in shape that was evidenced by rippling along the edges.

Differences in the effect of fresh water compared to the effect of seawater are observed by comparing graphs of the same sample in the two different mediums. For all samples tested the amount of degradation observed was greater for samples immersed in fresh water. This behavior is not entirely unexpected since Cassidy and Rolls [3] previously reported similar results for Neoprene WRT. A possible explanation for the existence of a difference is that water is the primary species diffusing into the polymer. This implies that the amount of interaction would be less for seawater since the thermodynamic activity of water in seawater is less than 1.00 due to the presence of salts in solution. A surprising result is that the amount of difference between fresh water and seawater interactions is not consistent but instead varies from polymer to polymer.

For several polymers the degree of interaction was considerably higher in fresh water at 60 and 80°C than would be expected based on the results at other temperatures. Samples of polychloroprene (Neoprene W), natural rubber, and epoxide (EPON VI) have curves (Figs. 4, 5, 25, and 34) at 60 and 80°C with slopes greater than the curves at the other temperatures. One possible explanation of this behavior is a reaction between water and a component of the elastomeric material which occurs to a significant extent at elevated temperatures. The reaction may not occur in seawater because of interference of the salts present in solution.

It is apparent in Figs. 20, 21, 22, 31, and 32 that polyurethane and polycarbonate reached their solubility limit since the curve for each temperature converges to a constant value. Although each curve for polycarbonate approaches a limiting value, the curves do not all converge to the same value. This implies that there is a temperature dependence of the water solubility limit for polycarbonate. Polyurethane exhibits the same behavior in fresh water but has a solubility limit independent of temperature in seawater.

As seen in Figs. 17 and 18, silicone rubber (V121) undergoes entirely different processes in fresh water and in seawater. In fresh water, it appears to undergo a diffusion-controlled process since the log-log plot of weight change versus time is similar to the graph Neoprene W, Fig. 5. Silicone rubber exposed to seawater shows complex weight change behavior indicating several processes occurring simultaneously. This difference implies the existence of interactions with the salts present in seawater.

Chlorobutyl (H862A) is affected by fresh water and seawater via a diffusion process, under most conditions. However, chlorobutyl exhibited complex behavior at 10°C (see Figs. 11 and 12). There is apparently another process competing with diffusion at lower temperatures. These results were confirmed by repeating the test for fresh water at 10°C.

Of the elastomers studied, six showed behavior indicative of a diffusion controlled process (the slope of the log-log plot of fractional weight change versus time was equal to 0.5). The remaining samples showed more complex behavior with several processes occurring simultaneously. The six samples exhibiting signs of a diffusion process are Neoprene W, Neoprene 5112, Chlorobutyl H862A, and natural rubber immersed in seawater and Neoprene W and natural rubber in fresh water. Since the natural rubber samples were tested at only two or three temperatures, there was insufficient data to obtain a reliable calculation of the energy of activation.

Figures 1, 2, and 3 are graphs of the natural logarithm of k versus the reciprocal absolute temperature for Neoprene W, Neoprene 5112, and Chlorobutyl H862A, respectively. The values for the activation energy and the statistical factor obtained from these graphs are given in Table 2. Predictions of the lifetime of a component can be made by substituting the appropriate values into Eq. (12).

Table 2: Activation Energy of Diffusion

GENERIC TYPE	FORMULATION	TYPE OF EXPOSURE	E_a	A
Polychloroprene	Neoprene W	seawater	58.6 kJ/mol	2.49×10^3
		water	56.4 "	2.02×10^3
Polychloroprene	Neoprene 5112	seawater	67.8 "	5.69×10^3
Chlorobutyl	H862A	seawater	82.8 "	1.65×10^6

Since the change in weight of a sample is not an absolute test, it cannot be used exclusively to predict the useful lifetime of a polymer. However, failure in an end-use test is very probably related to the weight change of the polymer on exposure to water. This allows a prediction of the amount of time until the polymer fails. For example, if a given, significant loss of tensile strength occurs with a 10% weight gain (must be determined experimentally) for Neoprene W, then the time it would take for failure to occur in seawater at 25°C would be 8.6 years. This was calculated using Eq. (12). For polymers that do not interact by a diffusion process, estimates of the lifetime can be made using the graphs in Appendix B.

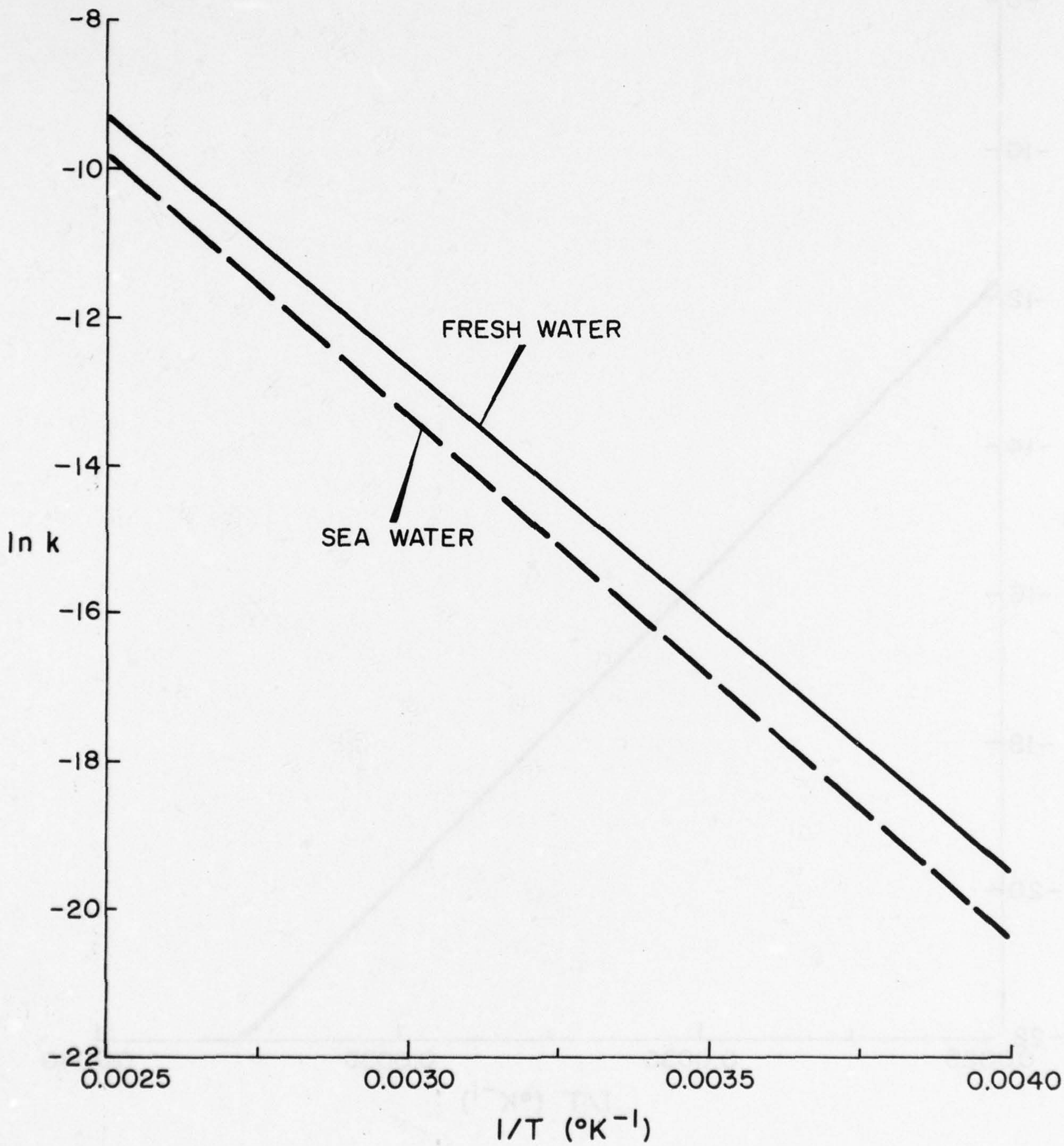

Fig. 1 - Polychloroprene (Neoprene W)

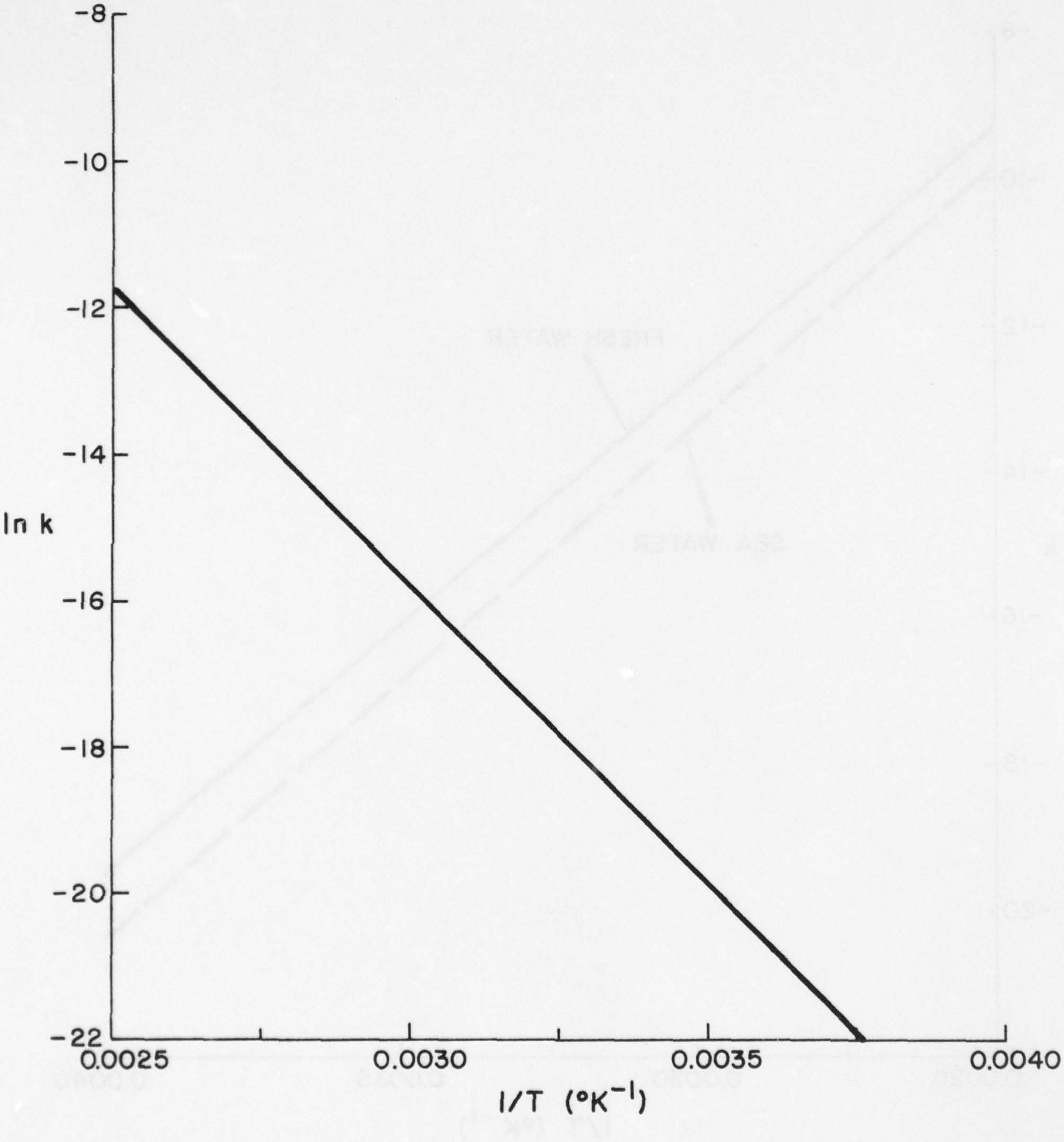

Fig. 2 - Polychloroprene (Neoprene 5112) Exposed to Seawater

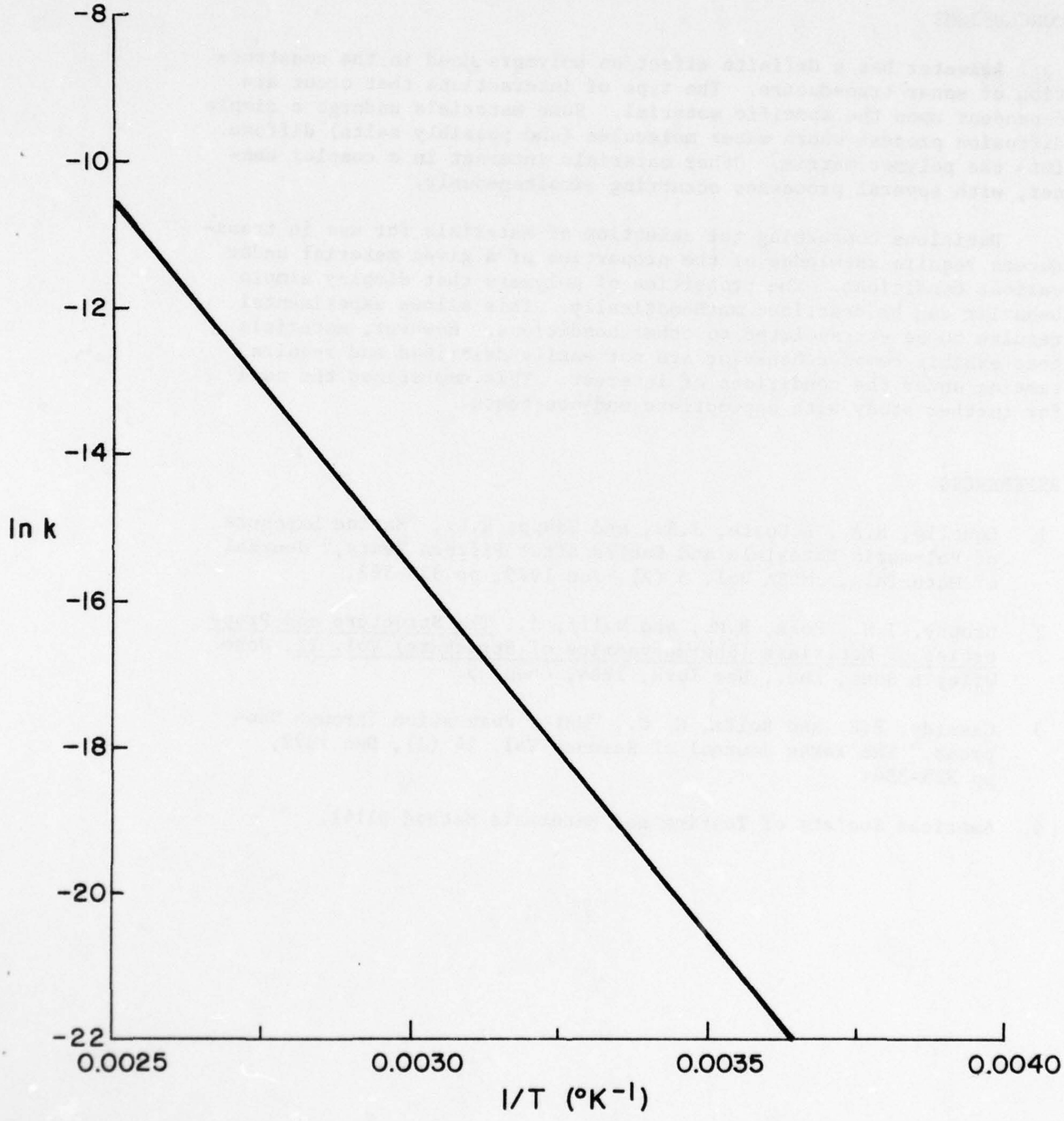

Fig. 3 - Chlorobutyl (H862A) Exposed to Seawater

CONCLUSIONS

Seawater has a definite affect on polymers used in the construction of sonar transducers. The type of interactions that occur are dependent upon the specific material. Some materials undergo a simple diffusion process where water molecules (and possibly salts) diffuse into the polymer matrix. Other materials interact in a complex manner, with several processes occurring simultaneously.

Decisions concerning the selection of materials for use in transducers require knowledge of the properties of a given material under various conditions. The properties of polymers that display simple behavior can be described mathematically. This allows experimental results to be extrapolated to other conditions. However, materials that exhibit complex behavior are not easily described and require testing under the conditions of interest. This emphasizes the need for further study with appropriate end-use tests.

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1 Conolly, R.A., DeCoste, J.B., and Gaupp, H.L., "Marine Exposure of Polymeric Materials and Cables after Fifteen Years," Journal of Materials, JMLSA Vol. 5 (2), Jun 1970, pp 339-362.

2 Brophy, J.H., Rose, R.M., and Wulff, J., The Structure and Properties of Materials (Thermodynamics of Structure) Vol. II, John Wiley & Sons, Inc., New York, 1964, Chap. 5.

3 Cassidy, P.E. and Rolls, G. C., "Water Permeation Through Neoprene," The Texas Journal of Science Vol. 24 (3), Dec 1972, pp 325-334.

4 American Society of Testing and Materials Method D1141.

APPENDIX A

EXPERIMENTAL TECHNIQUES

The tests were performed by immersing samples of the polymer in water (seawater) that was at the test temperature. The elastomers were molded and cured from stock compounded uncured materials. The test samples had dimensions of 25×25×3.94 mm.

Deionized water was used for the samples immersed in water. The substitute seawater used was prepared as described in ASTM Method D1141 [4]. The solution used did not include heavy metals.

The hardness was measured with a Shore Hardness Type "A2" Durometer. The thickness was measured with an Ames micrometer.

APPENDIX B

GRAPHS OF RESULTS

(See Figs. 4 through 36 on the following pages.)

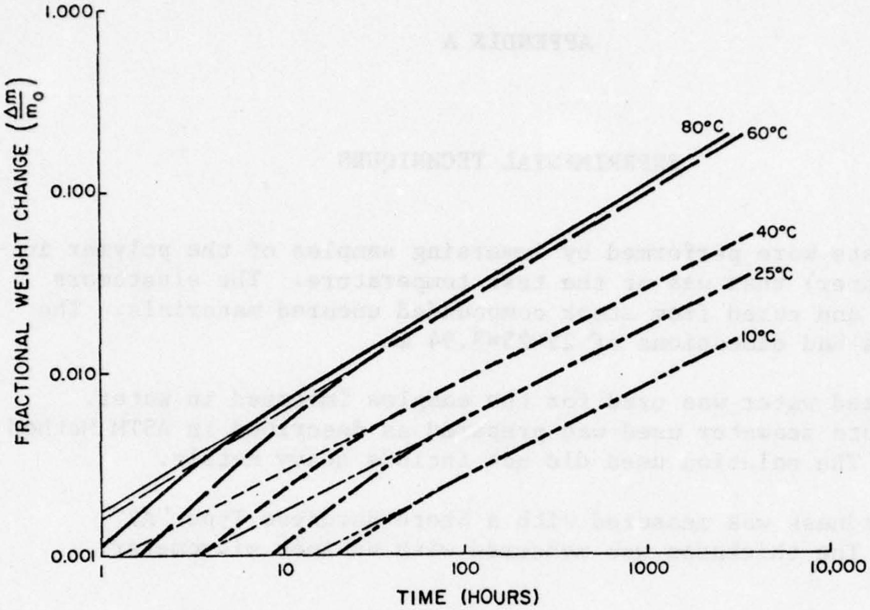

Fig. 4 - Polychloroprene (Neoprene W) Exposed to Water

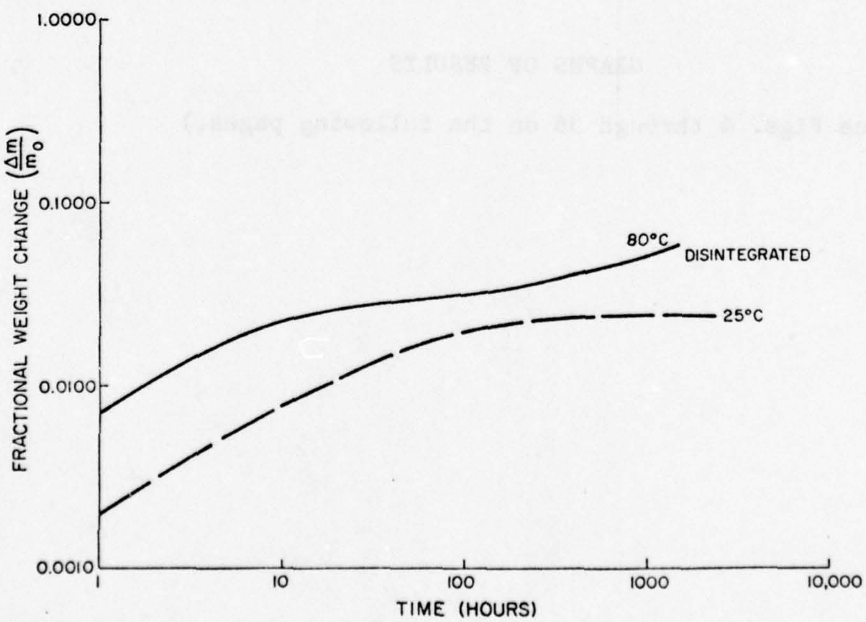

Fig. 5 - Polychloroprene (Neoprene W) Exposed to Seawater

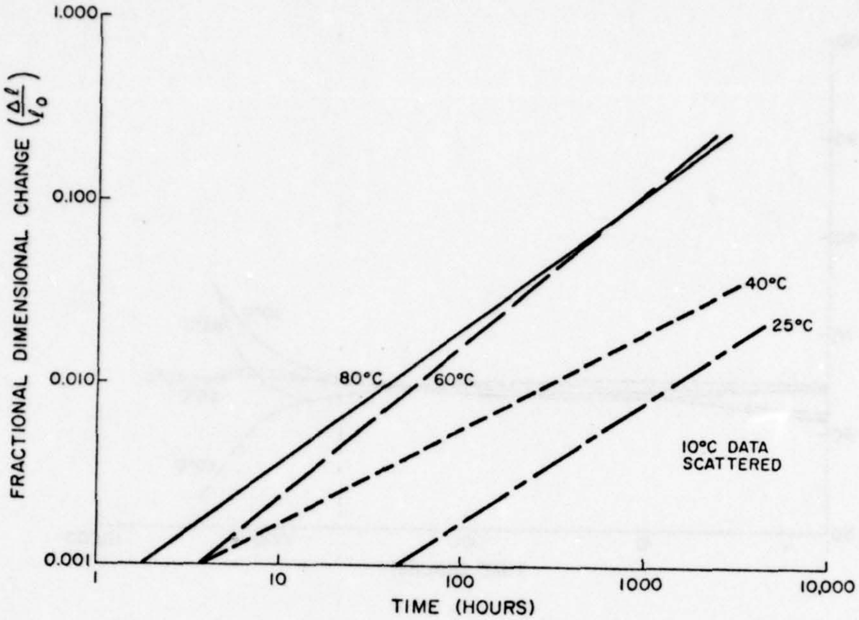

Fig. 6 - Polychloroprene (Neoprene W) Exposed to Water

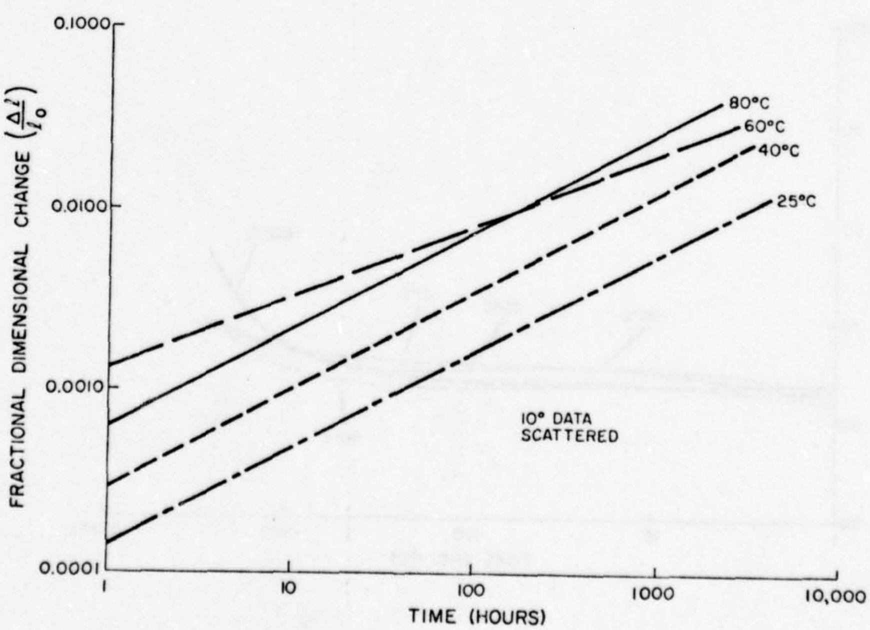

Fig. 7 - Polychloroprene (Neoprene W) Exposed to Seawater

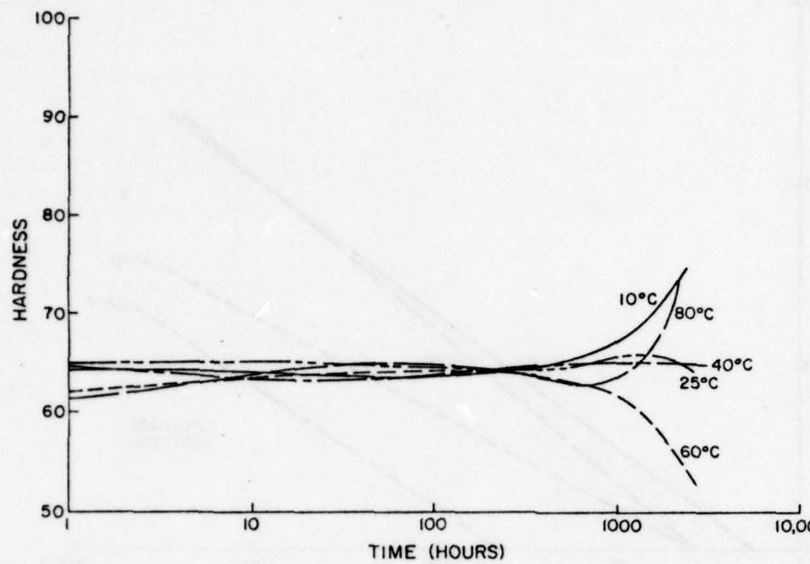

Fig. 8 - Polychloroprene (Neoprene W) Exposed to Water

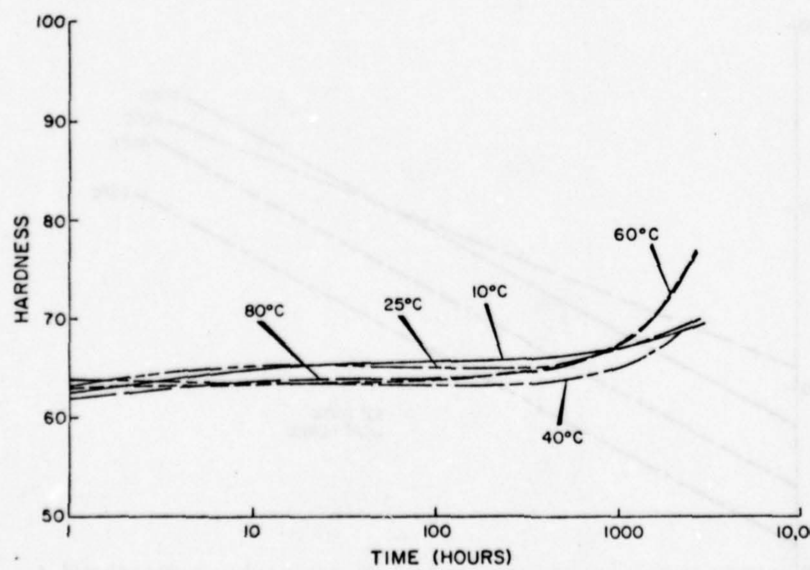

Fig. 9 - Polychloroprene (Neoprene W) Exposed to Seawater

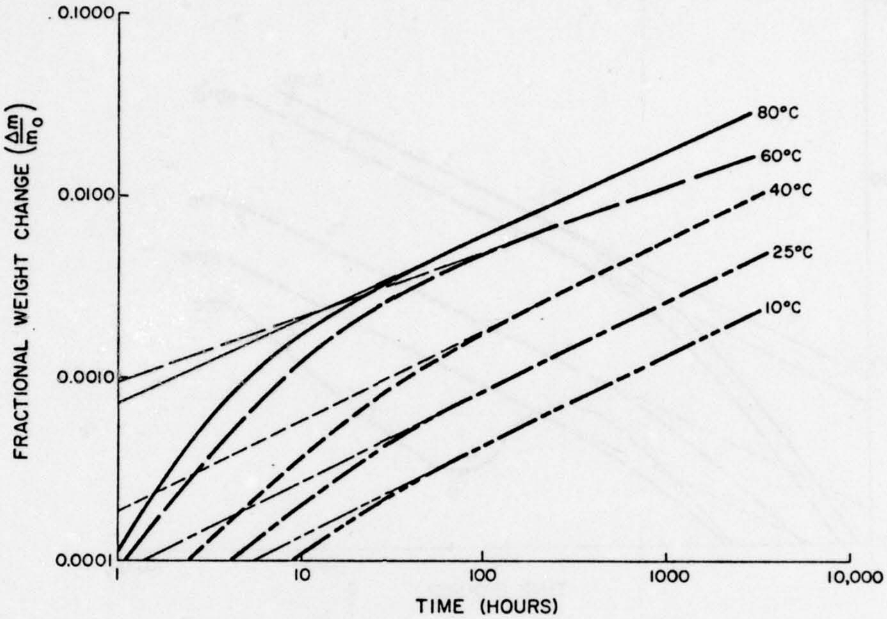

Fig. 10 - Polychloroprene (Neoprene 5112) Exposed to Seawater

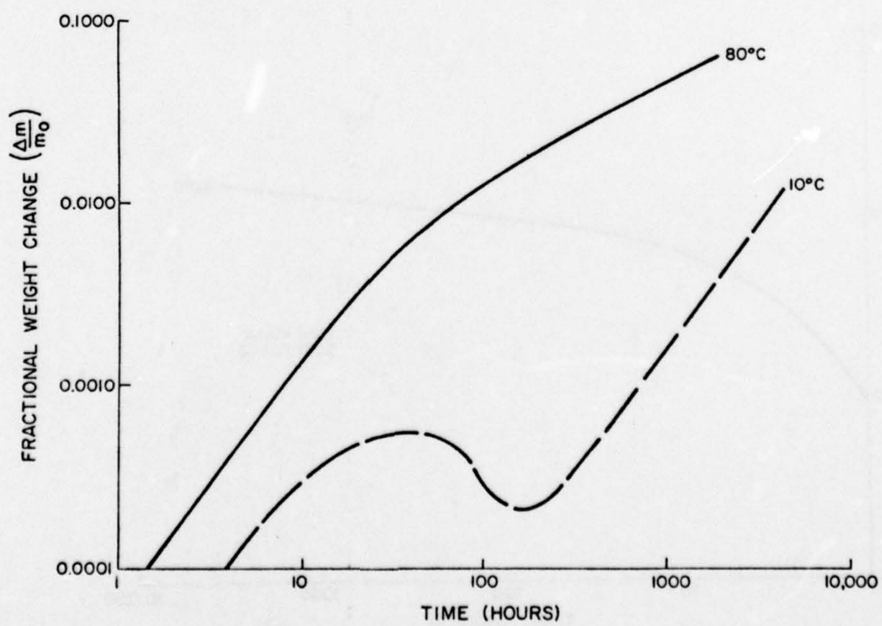

Fig. 11 - Chlorobutyl (H862A) Exposed to Water

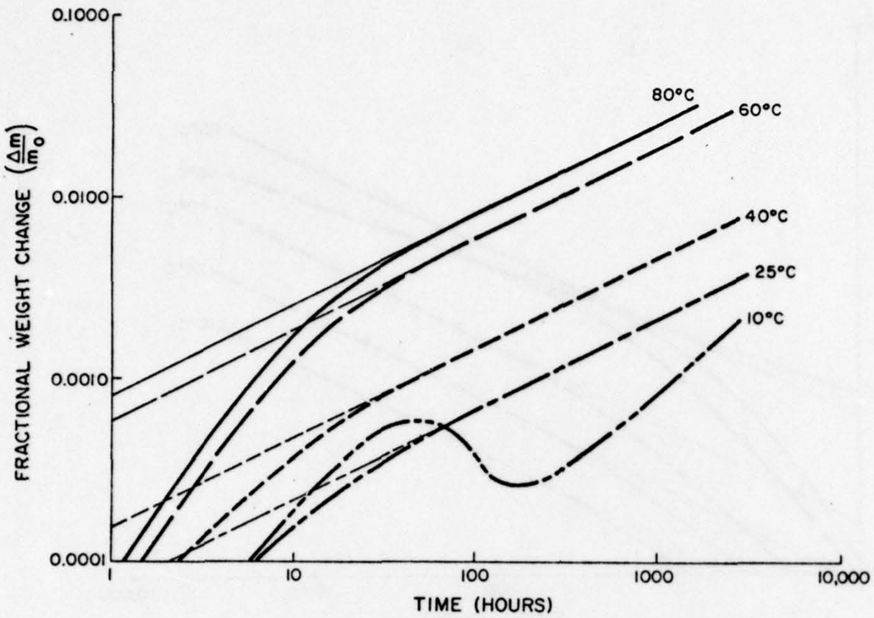

Fig. 12 - Chlorobutyl (H862A) Exposed to Seawater

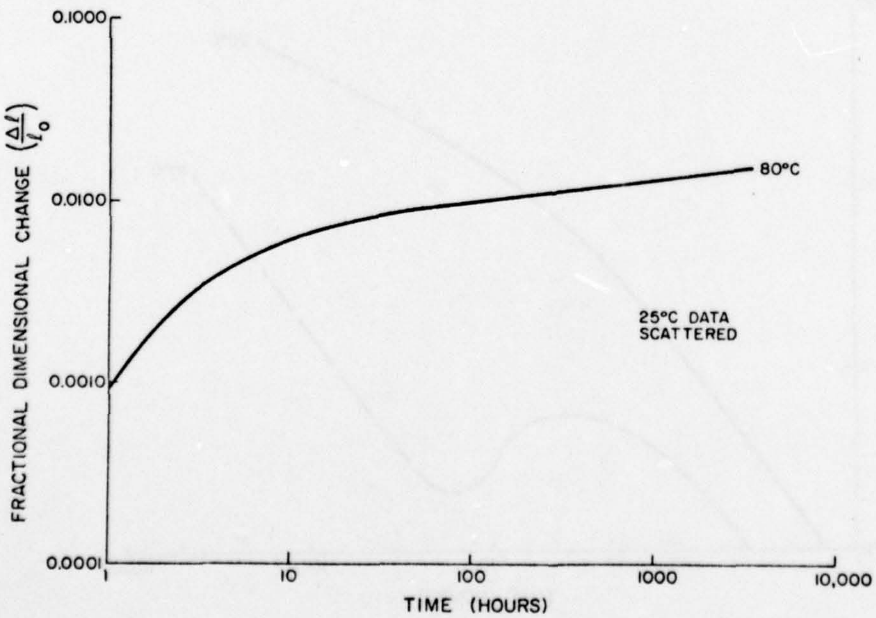

Fig. 13 - Chlorobutyl (H862A) Exposed to Seawater)

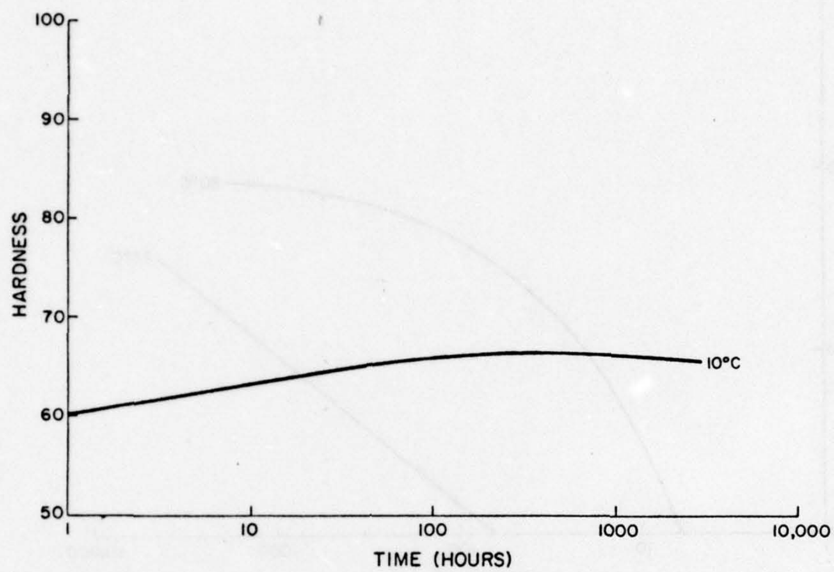

Fig. 14 - Chlorobutyl (H862A) Exposed to Water

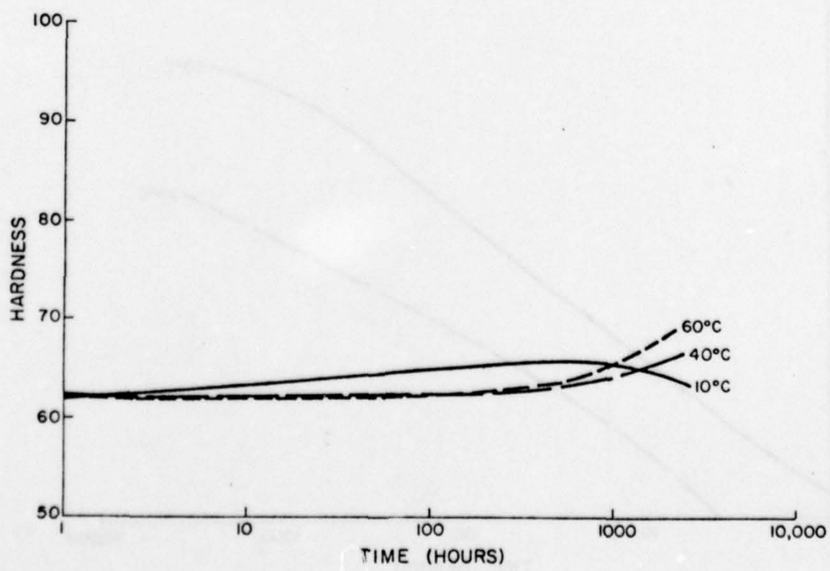

Fig. 15 - Chlorobutyl (H862A) Exposed to Seawater

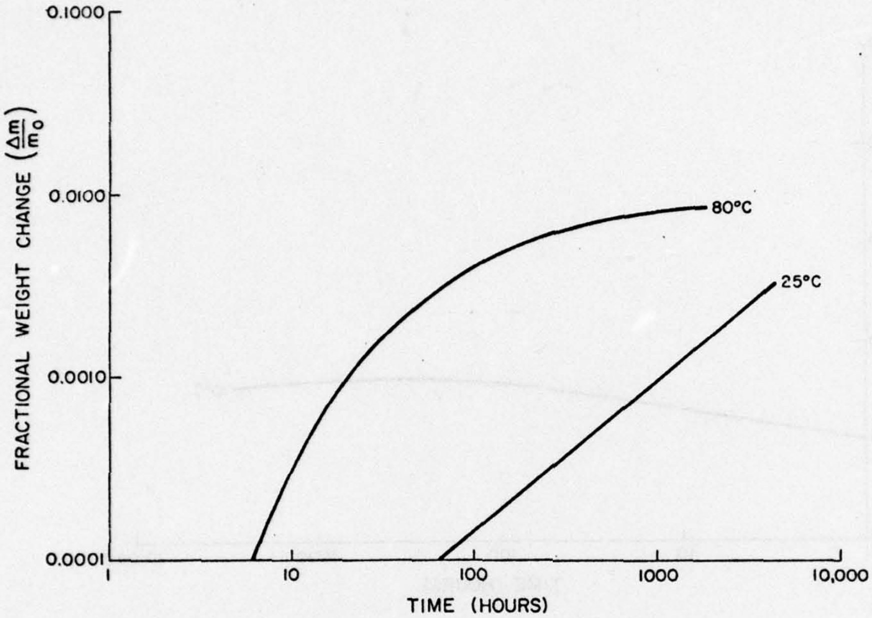

Fig. 16 - Butyl (B252) Exposed to Seawater

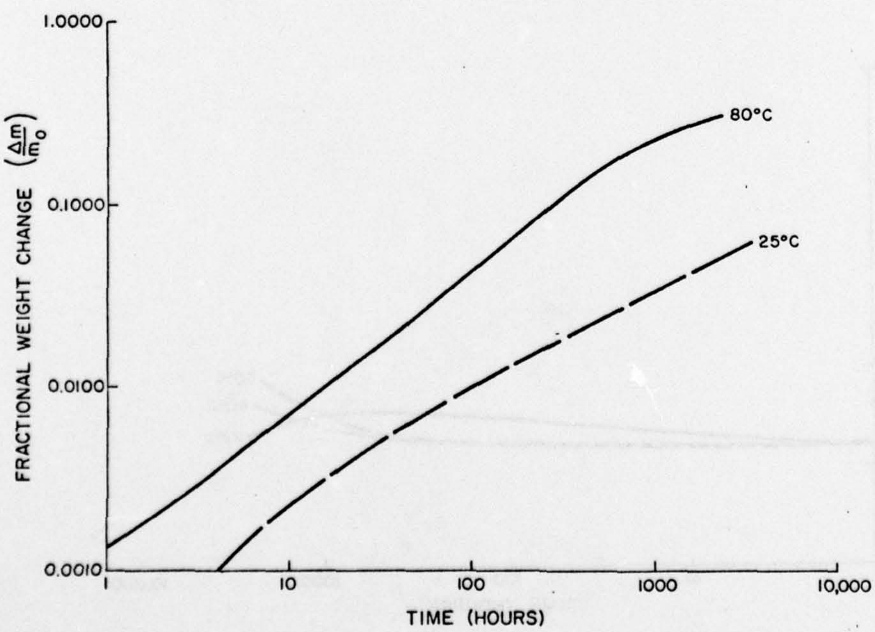

Fig. 17 - Silicone Rubber (V121) Exposed to Water

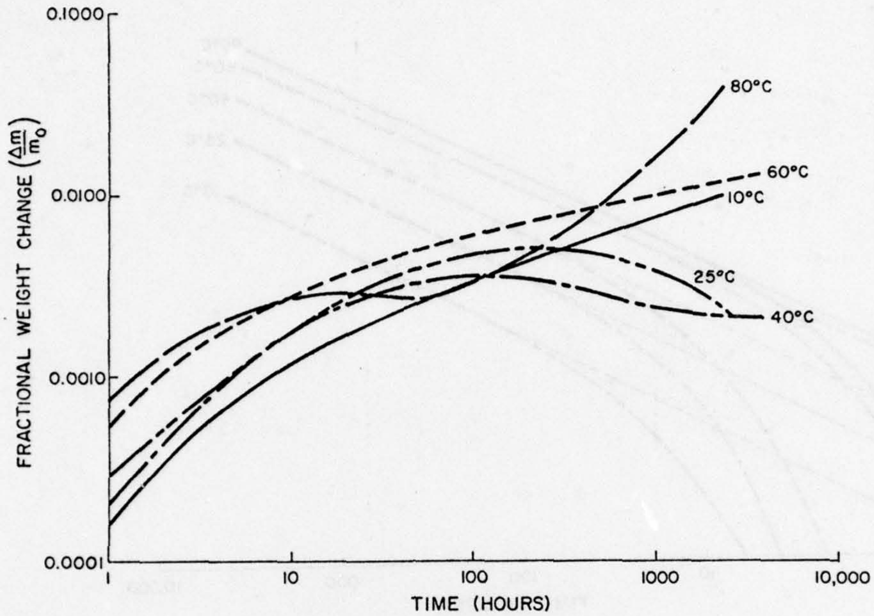

Fig. 18 - Silicone Rubber (V121) Exposed to Seawater

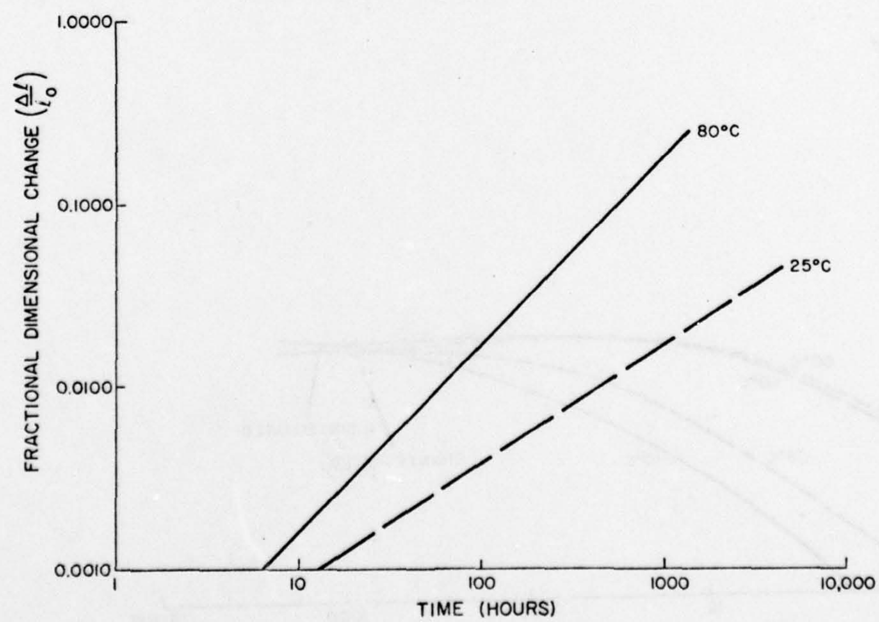

Fig. 19 - Silicone Rubber (V121) Exposed to Water

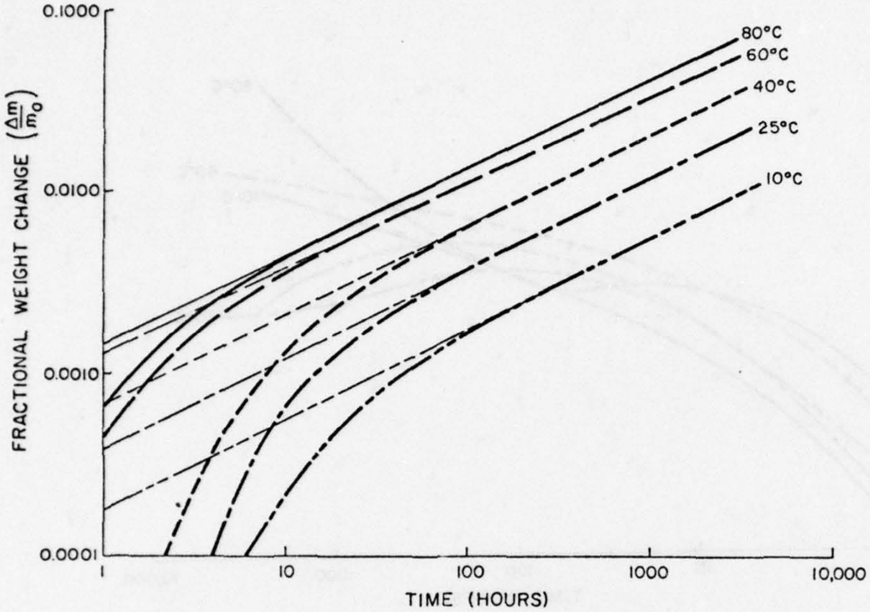

Fig. 20 - Polyurethane (PRC 1538) Exposed to Water

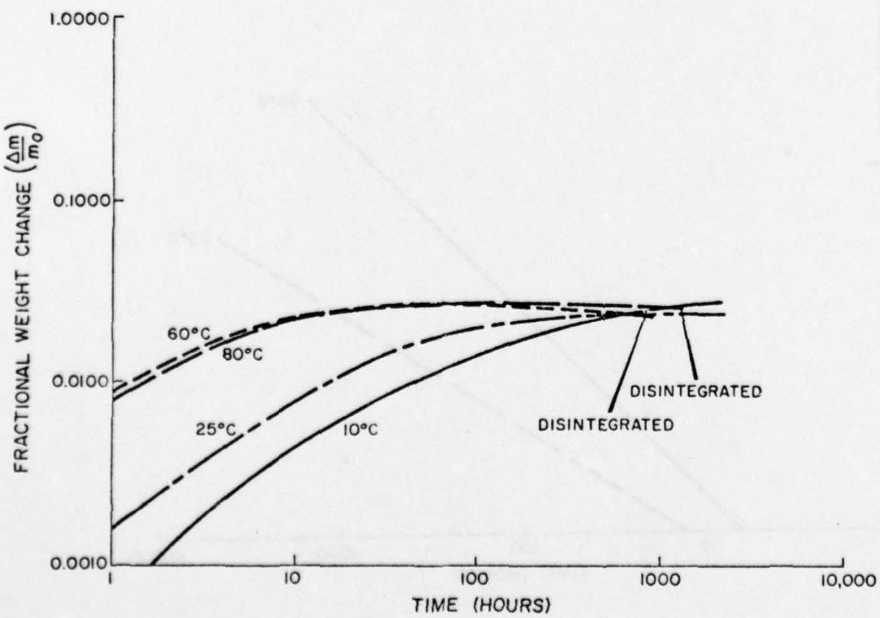

Fig. 21 - Polyurethane (PRC 1538) Exposed to Seawater

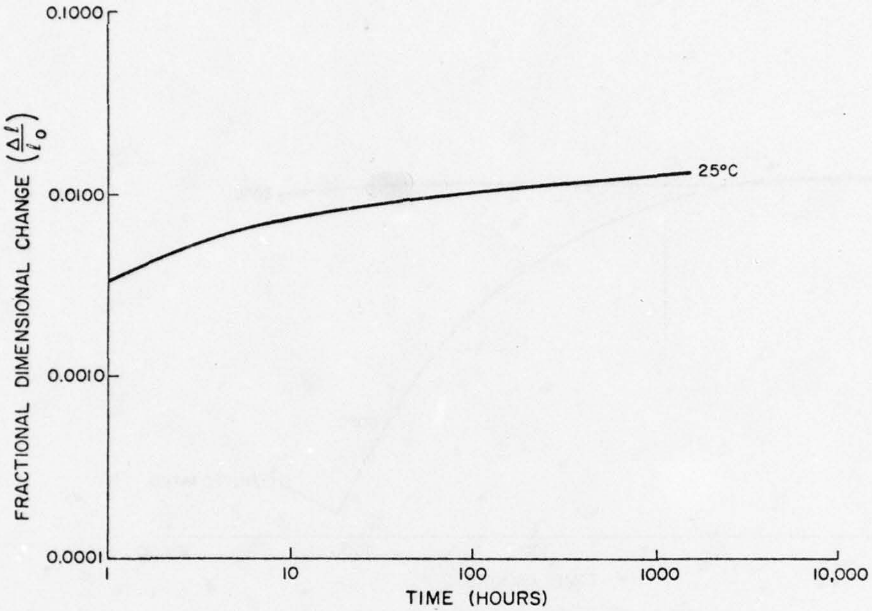

Fig. 22 - Polyurethane (PRC 1538) Exposed to Seawater

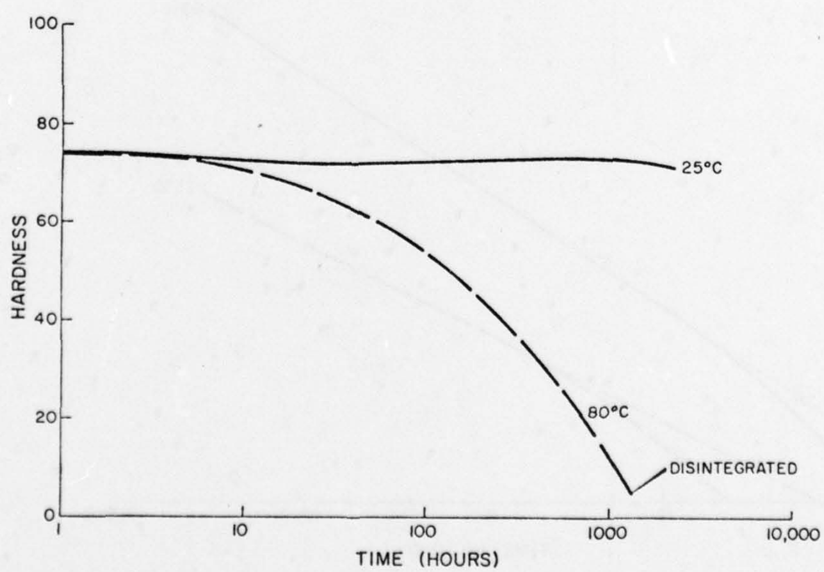

Fig. 23 - Polyurethane (PRC 1538) Exposed to Water

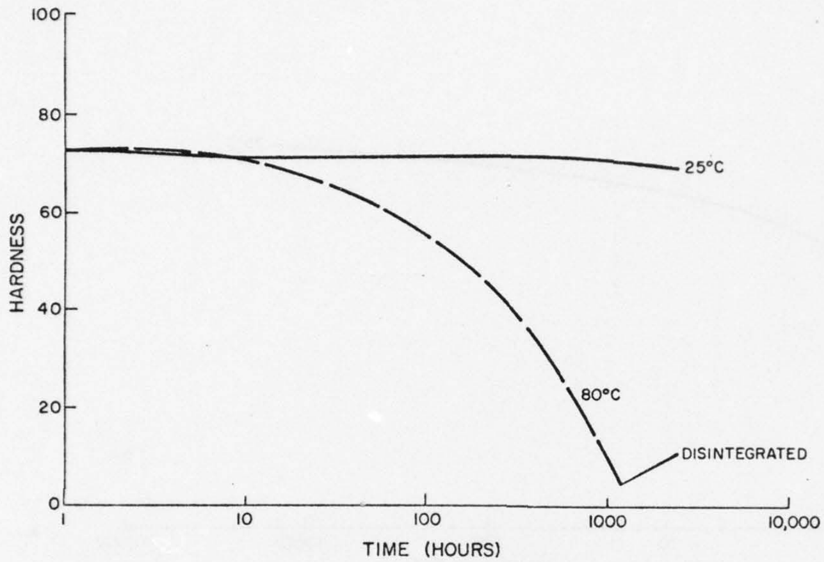

Fig. 24 - Polyurethane (PRC 1538) Exposed to Seawater

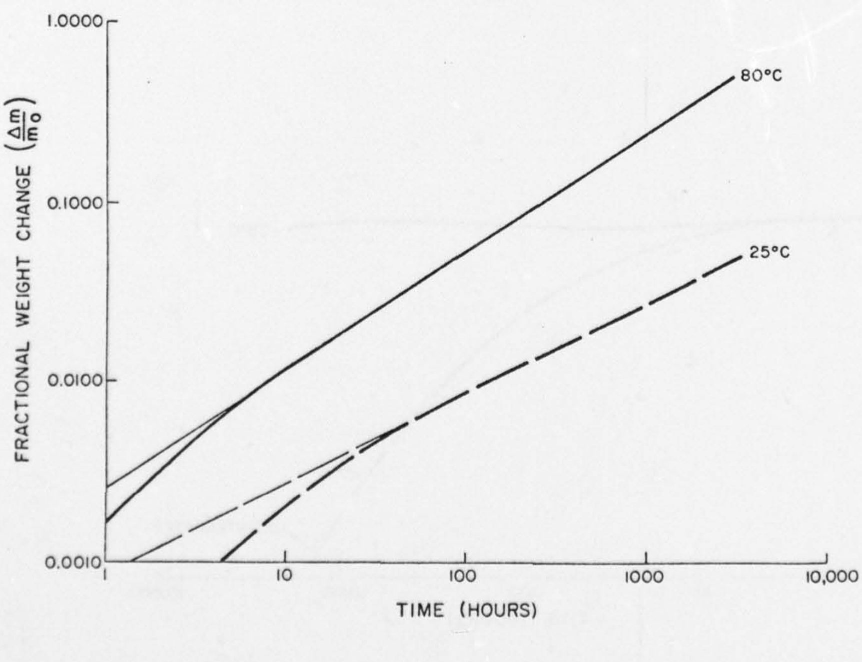

Fig. 25 - Natural Rubber (BFG 35007) Exposed to Water

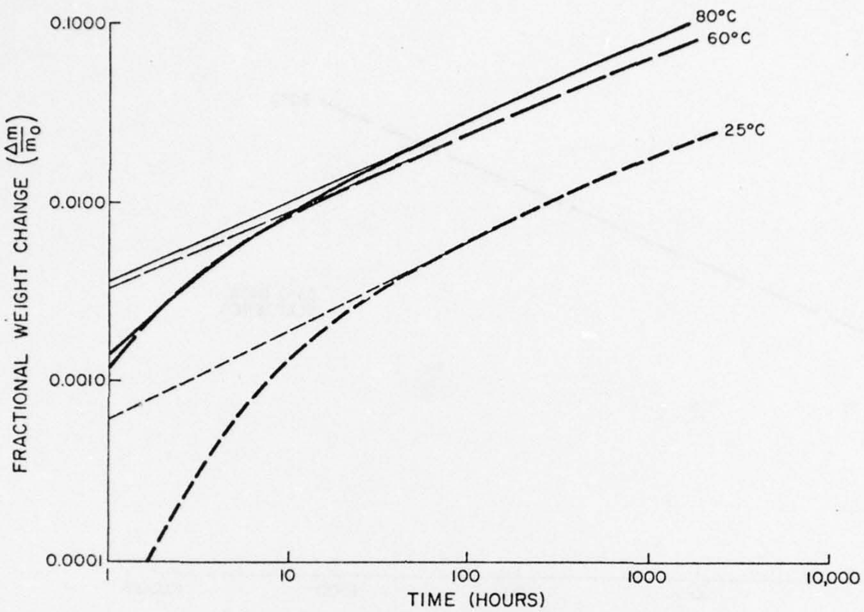

Fig. 26 - Natural Rubber (BFG 35007) Exposed to Seawater

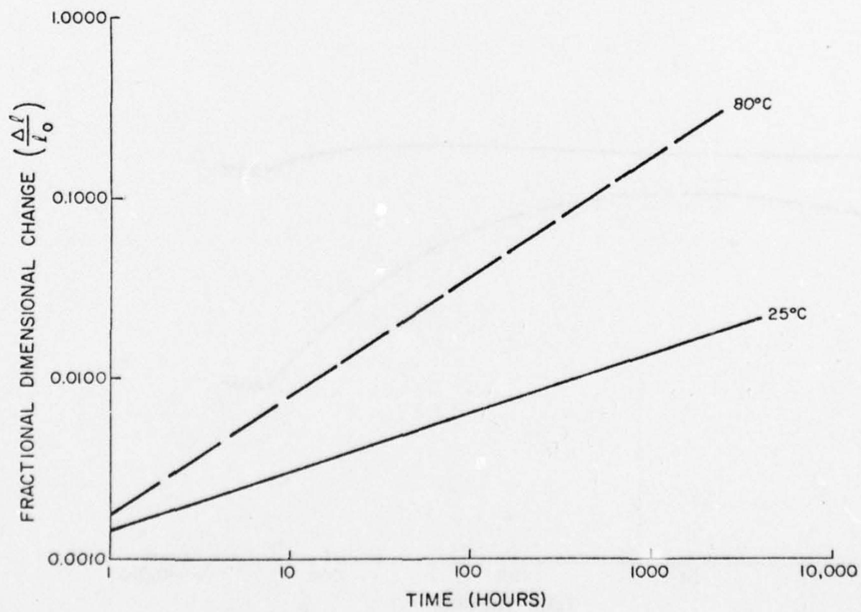

Fig. 27 - Natural Rubber (BFG 35007) Exposed to Water

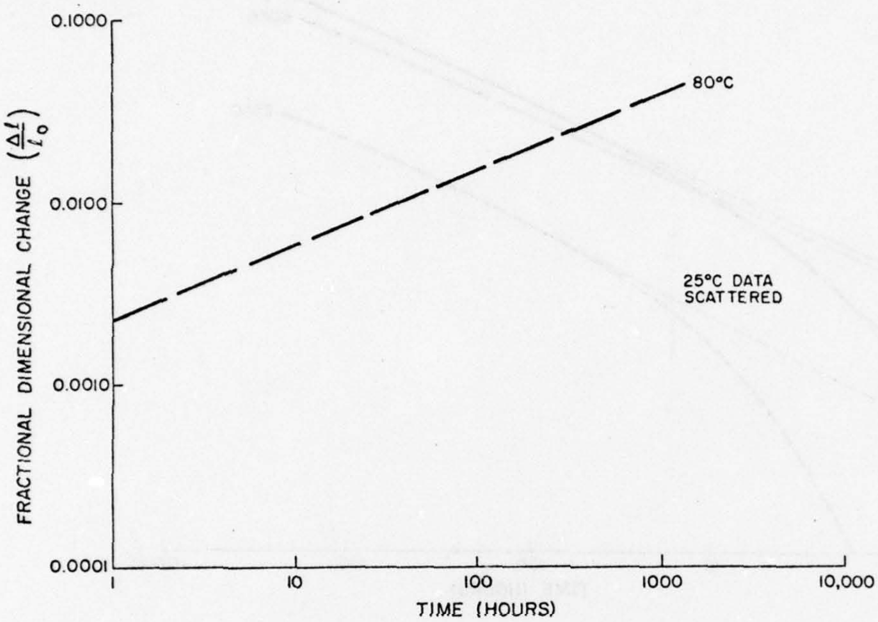

Fig. 28 - Natural Rubber (BFG 35007) Exposed to Seawater

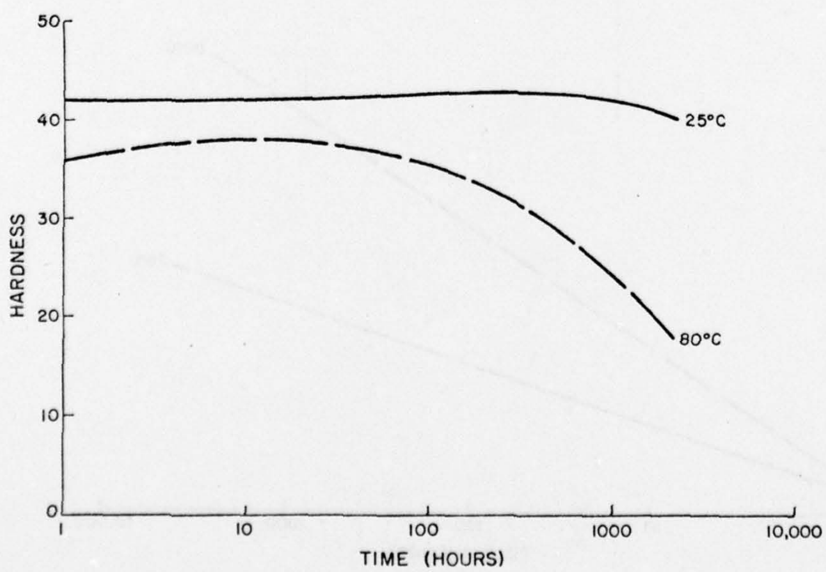

Fig. 29 - Natural Rubber (BFG 35007) Exposed to Water

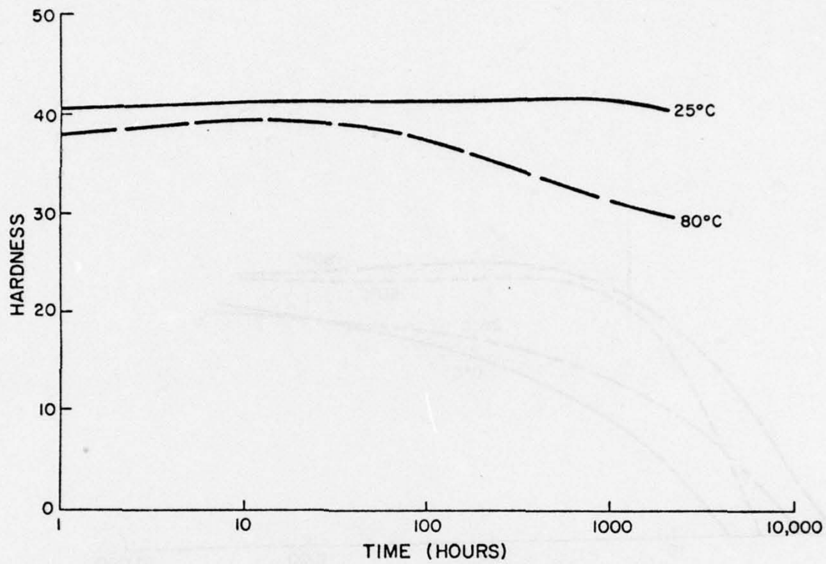

Fig. 30 - Natural Rubber (BFG 35007) Exposed to Seawater

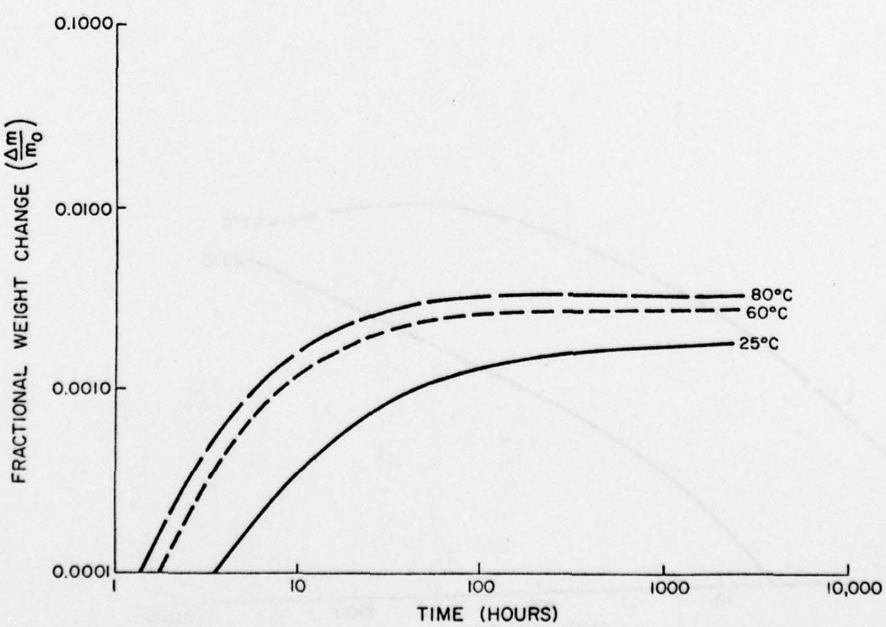

Fig. 31 - Polycarbonate (Lexan) Exposed to Water

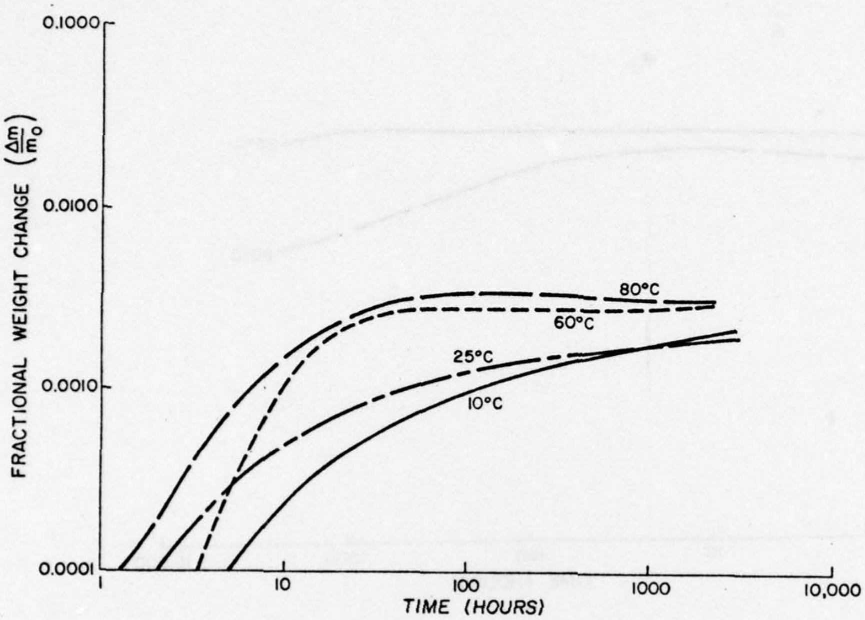

Fig. 32 - Polycarbonate (Lexan) Exposed to Seawater

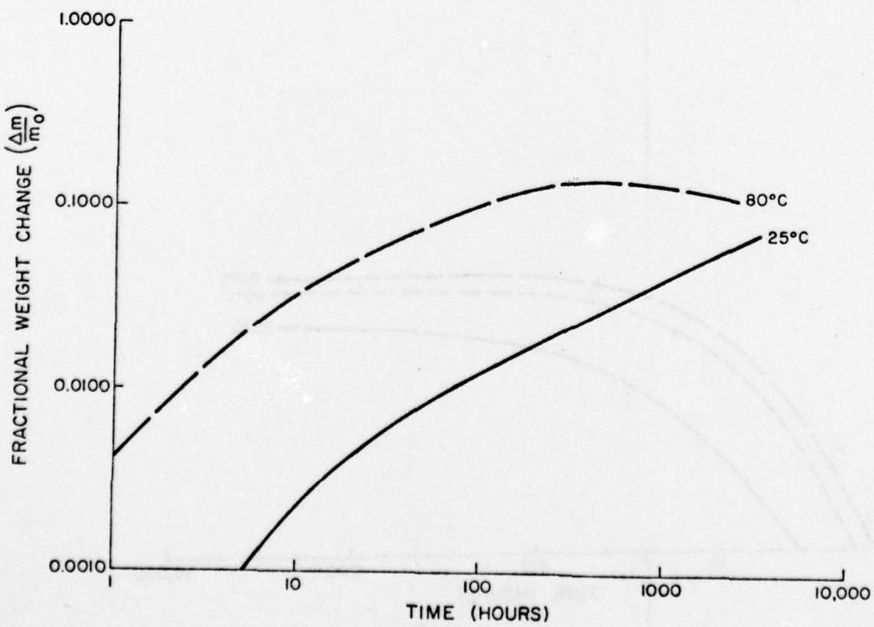

Fig. 33 - Epoxy (EPON VI) Exposed to Water

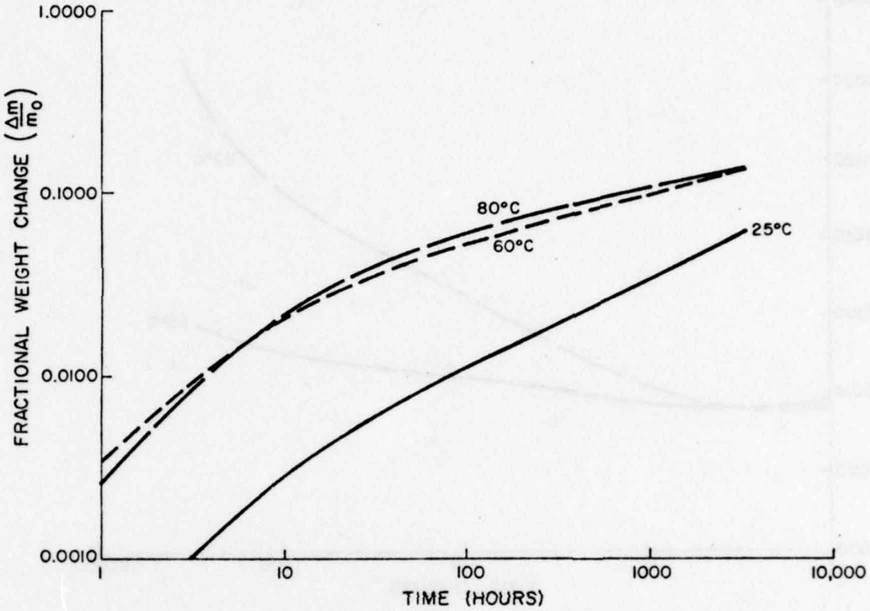

Fig. 34 - Epoxy (EPON VI) Exposed to Seawater

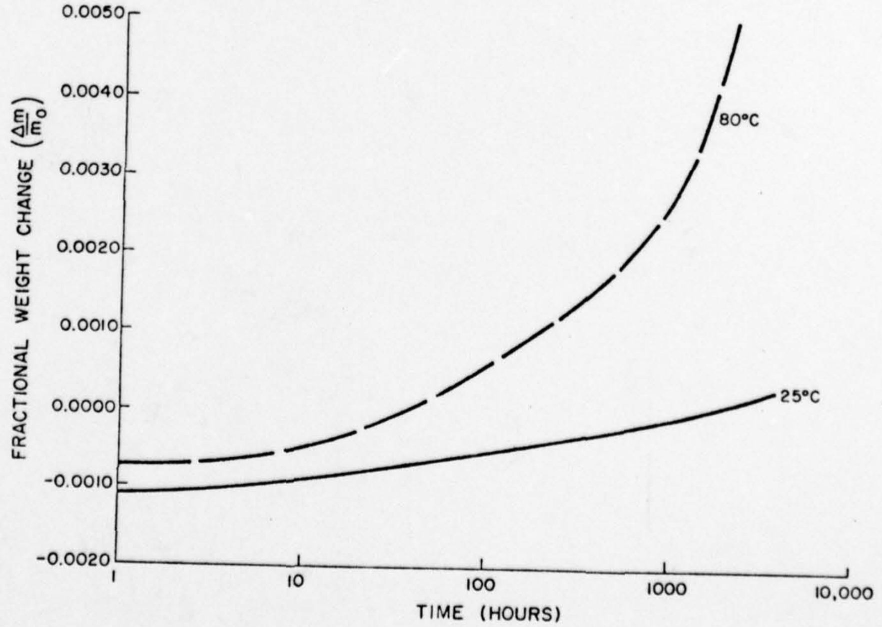

Fig. 35 - Nylon Exposed to Water

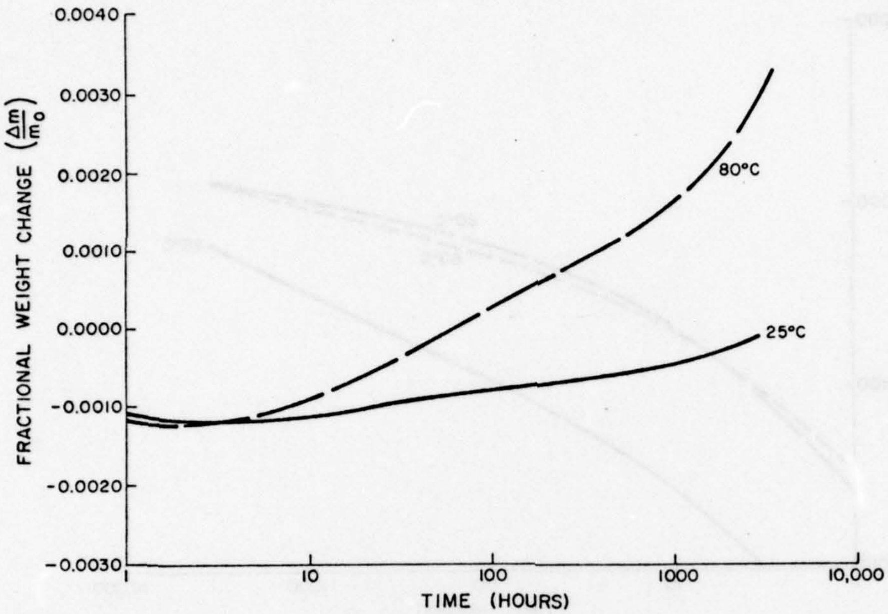

Fig. 36 - Nylon Exposed to Seawater