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ELECTROCHEMICAL TECHNOLOGY CORP SEATTLE WASH
A STUDY OF TRANSPORT PROCESSES AND INITIATION OF CORROSION UNDE--ETC(U)
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F49620-76-C-0029

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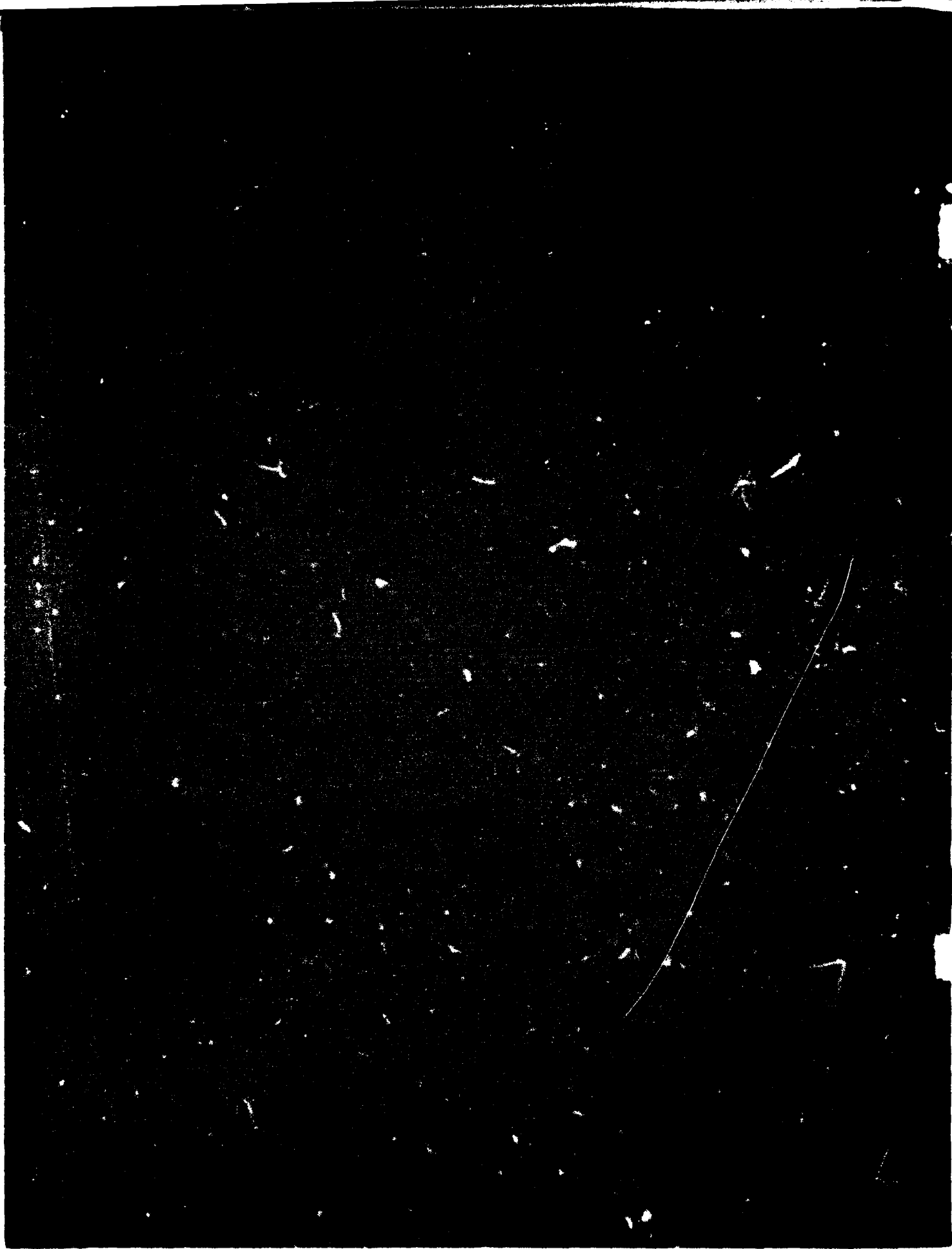
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19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER (18) AFOSR-TR-80-0028	2. GOVT ACCESSION NO.	3. PERFORMER'S CATALOG NUMBER	
4. TITLE (and Subtitle) (6) A Study of Transport Processes and Initiation of Corrosion Under Paint Films.		5. TYPE OF REPORT & PERIOD COVERED (9) 1 Oct 76 - 30 Sep 79 Final Report, 1 Oct 76 - 30 Sep 79	
6. AUTHOR(s) (10) Theodore R. Beck and Robert T. Ruggeri PL		7. PERFORMING ORG. REPORT NUMBER 30 Sep 79	
8. CONTRACT OR GRANT NUMBER(s) (15) F49620-76-C-0029		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) 61102F (17) 2363/A2 A2	
10. PERFORMING ORGANIZATION NAME AND ADDRESS Electrochemical Technology Corp./ 3935 Leary Way N.W. Seattle, WA 98107		11. CONTROLLING OFFICE NAME AND ADDRESS (11) Air Force Office of Scientific Research/NC Bolling AFB, Bldg. 410 Washington, D.C. 20332	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 501		13. REPORT DATE Nov 1979	
		14. NUMBER OF PAGES 49	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) corrosion, diffusion, filiform corrosion, mathematical model, paint, polyurethane, sodium chloride, transport processes, water permeation			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Combating corrosion of airplane structure is a large and increasing cost to the Air Force. Fundamental knowledge of how protective coatings function is required in order to develop improved coating systems. This research was directed to obtain quantitative knowledge of mass transport and kinetic mechanisms that result in initiation of corrosion under paint films. Mathematical modeling of transport processes and electrochemical tests on paint films were conducted concurrently. Coating systems of current use in			

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the Air Force, polyurethane and epoxy, were examined. Experiments were conducted with detached films and with films on aircraft alloy aluminum and iron substrates.

A review of paint literature indicated that there are many parameters which may be important in understanding how paint protects metal surfaces from corrosion. Most research in this area has been focused on a single aspect such as osmotic pressure or electrolyte concentration, and there was a clear need to establish a broader framework for analysis of paint performance. To this end a one-dimensional model of the mass transport through paint films was developed. All mobile species; ionic, solute, and solvent, were included. The paint phase was considered to be a concentrated, multicomponent solution for which appropriate flux equations were written. By combining these flux equations with the usual species continuity equations, and with the inclusion of an equation of state and the electroneutrality condition, a complete set of coupled nonlinear differential equations was obtained. The solution of this equation set was accomplished by an iterative technique which allowed for metal-surface kinetic effects through the boundary conditions. This model has identified a complete set of parameters relevant to the corrosion process (diffusion coefficients, transference numbers, etc.).

An extensive series of experiments was conducted to determine diffusion coefficients, transference numbers, water absorption, and other parameters for polyurethane paint as required by the model. The permeability of water was found to be fast

$$(P_{H_2O} \approx 10^{-12} \text{ mole/cm}^2\text{s for a } 7 \times 10^{-3} \text{ cm thick film and}$$

$$\Delta C_{\text{bulk}} = 0.02 \text{ mole/l})$$

so that only a few minutes is required for penetration. The permeability of ions is extremely low

$$(P_{Na^+} \approx 10^{-15} \text{ mole/cm}^2\text{s for a } 7 \times 10^{-3} \text{ cm thickness and}$$

$$\text{a potential difference } \Delta\phi = 1.5 \text{ V})$$

so that ionic transport appears to be negligible. Insertion of measured parameter values into the model has given consistent calculational results.

Filiform corrosion is often observed under coatings on aircraft structures. A new mechanism was developed which accounts for the unidirectional propagation and other aspects of filiform growth. Experimental data and mass transport calculations support the concept that oxygen and water reach the active head of the filiform by diffusion through the porous tail.

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FINAL TECHNICAL REPORT
AFOSR (F49620-76-C-0029)

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3. TITLE:

A Study of Transport Processes and Initiation of Corrosion
Under Paint Films

4. COSTS AND FISCAL YEAR SOURCE:

\$48,370, FY77; \$45,186, FY78; \$47,117, FY79.

5. OTHERS INVOLVED:

Dr. Robert T. Ruggeri, a chemical engineer, carried out the mathematical modeling and supervised the experimental work. He was guided in the mathematical modeling effort by Professor Douglas N. Bennion who was at Electrochemical Technology Corp. on industrial leave from UCLA during the academic year 1977-1978. Olwen M. Morgan and Sandra G. Chan, chemists, and Raymond Carveth and Michael LaScala, chemical technicians, assisted in the experimental work.

6. SUMMARY OF PROGRESS:

Corrosion of metals coated with paint films has previously been extensively studied, but a general quantitative treatment was unavailable. To this end, general mathematical and computer models were developed to quantitatively describe the diffusion and migration of mobile species (solvents and ions) through polymer films. The models required thermodynamic data and transport parameters which were not available. A series of experiments was therefore performed to obtain this required information using a single polyurethane paint type. Based on these data a test of the applicability of the models was conducted. New thermodynamic data were obtained, and the applicability of the model was supported; however, because the available thermodynamic data are incomplete, a critical test of the

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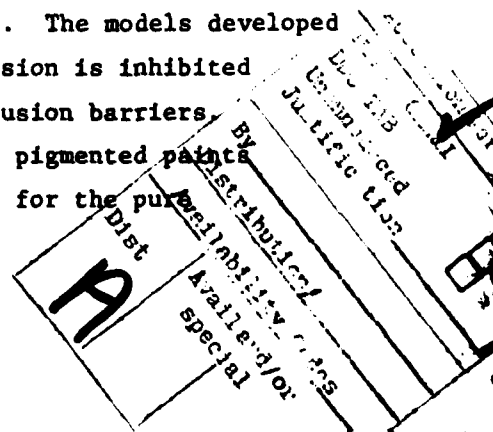
model remains to be performed. The experiments indicate that the diffusion coefficient of ions through polyurethane is exceedingly low ($D_{Na^+} < 10^{-9} \text{ cm}^2/\text{s}$) and that under most conditions the transport of ions through the paint can be ignored. The diffusivity of water was found to be $3.2 \times 10^{-8} \text{ cm}^2/\text{s}$ with a solubility, at unit water activity and 21°C , of $1.3 \times 10^{-2} \text{ g-water/g-paint}$. Under normal field conditions it is likely the ions beneath the paint were present before the coating was applied or they entered through defects, and the corrosion is limited by either the oxygen or water diffusion through the paint.

As a result of the studies of the diffusional properties of paint films, filiform corrosion was investigated. This investigation revealed a new mechanism for filiform growth: diffusion of oxygen and water toward the head through a porous tail. This new mechanism explains for the first time the major features of filiform corrosion. Discussion of the work accomplished follows.

6.1 Introduction

Corrosion of airplane structure is a costly problem for the Air Force. Coatings have long been recognized as one method through which this cost can be reduced. Despite this fact, there has been little research conducted investigating the mechanisms through which coatings protect metal surfaces. Obviously, one way paints protect is by presenting a barrier to diffusion of ions and solvents, primarily water. Another way paint might protect metals is by affecting surface kinetics of the corrosion reactions. This research was undertaken in an effort to elucidate the mechanisms of the initiation of corrosion beneath paint films.

Usually the rate of metallic corrosion is controlled by mass transport through an oxide or other film rather than by kinetics. The models developed below have thus taken the point of view that the corrosion is inhibited by paint films primarily because the films act as diffusion barriers. Although this view may require modification for highly pigmented paints or those containing inhibitors, it is considered valid for the pure unpigmented binders studied here.



Many paint formulations could be chosen for study, but it was desirable to choose highly effective, modern, two-part polymers because such systems are presently used on airplanes. For this purpose a polyurethane (Desoto, Inc., Chemical Coatings Div., Berkeley, California, meeting Boeing material specification, BMS-10-60D-TYII, and Mil C-83286) and an epoxy (Koppers Co., Andrew Brown Div., Kent, Washington, BMS-10-11J-TYII) were chosen. These are both commercially important paints and were obtained from the Boeing Company, Seattle, Washington. Because the polyurethane was easier to handle, it initially received more attention than the epoxy. Later the polyurethane continued to receive added emphasis because of a need to fully-characterize the transport properties of at least one paint type.

The initial investigations were conducted on painted metal samples of 2024 and 7075 aluminum alloys. These systems gave erratic results, probably because of the metal-oxide paint interaction. In an attempt to minimize the effects of passivating oxide, iron and zinc were also tested. Although the iron and zinc systems produced more uniform results, they presented several problems as well. One of the most serious problems, from the standpoint of determining the transport properties of paint films, is the fact that the conditions (ion concentrations, pressure, etc.) at the paint-metal interface are unknown. Furthermore, these conditions cannot be considered uniform; thus the observed current densities, voltages, etc., are the result of average conditions at the paint-metal interface. For these reasons, most of the experiments were conducted on free paint films placed between two aqueous solutions of known concentration. The free films were produced by spraying the polymers on decal paper and then stripping in water. Curing was performed in the laboratory environment (average temperature, 21°C), and no special control was exercised over temperature or humidity.

A primary premise of this work is that corrosion is limited by mass transport, either reactants toward, or products away from the metal surface. The paint film is viewed as a homogeneous phase or solution in which all species other than the polymer are mobile, and the paint is considered to be capable of acquiring charge, i.e. contains ionizable sites. Thus, the paint possesses the same fundamental characteristics as an ion exchange membrane and is viewed as such. From this basis, a model describing the

mass transport through paint films has been developed (1). The model is one-dimensional and therefore inapplicable to multidimensional cases, such as blister formation, but is otherwise quite general in nature. It is, for instance, based on concentrated solution electrochemistry and is expected to be applicable under a much wider range of conditions than dilute solution theories.

6.2 Thermodynamic and Transport Properties of Polyurethane

A primary feature of a general theory is that it is based on a small number of well-specified assumptions. Less general theories require additional assumptions and can be thought of as subsets of the more general theory. Because of the general nature of the model presented here, certain implicit assumptions contained in previous theories can be ascertained. One of the important aspects of previous theories involves the implicit assumption of local equilibrium. The diffusion flux can generally be written in terms of a gradient in electrochemical potential ($\nabla\mu$). This necessitates a discussion of the definition of the electrochemical potential, strictly defined only under equilibrium conditions, in a non-equilibrium (diffusional) system. Usually local equilibrium is assumed inside a small region close to every point within the system. The practical implications of making this assumption are now clear; an equilibrium thermodynamic description of the system is required over the entire range of concentrations, temperature, and pressure encountered within the system. For corroding metals coated with paint films this involves detailed knowledge of a wet polymer system in which many ions are present. Unfortunately these data are not available from the literature and much time and effort have been spent during the course of this work evaluating thermodynamic properties of paint films.

Absorption of Water

Free films of polyurethane have been exposed to atmospheres of varying relative humidity and the weight change monitored on a Cahn gram electrobalance. The relative humidities were maintained by means of saturated

salt solutions. The results shown in Figure 1 are typical with percentage weight gain plotted versus relative humidity at $20^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The results of three experiments are shown in Figure 1. The first experiment illustrates the absorption isotherm of a polyurethane film soaked in distilled water for thirty days prior to the experiment. The absorption isotherm shows a total weight gain of about 1.5% at 100% relative humidity. This is the same as the total weight gain recorded after the test specimen had been soaked for thirty days in a hydrochloric acid ($\text{pH} = 3.0$) solution. The third experiment depicted in this figure shows the results obtained after the specimen was soaked in saturated sodium chloride solution for thirty days. The results indicate clearly that this type of polyurethane absorbs more water after being conditioned in a concentrated salt solution than before being conditioned. Furthermore, the effect of salt is apparently reversible since the distilled water experiment was performed after the saturated NaCl test while the dilute acid experiment preceded it. Apparently salt is absorbed by the polymer, and water is attracted to the same sites, perhaps driven by osmotic pressure. An alternate hypothesis might be that the salt opens up the polymer lattice, i.e., increases the free volume, and allows more water into the polymer. In any case, the variation in total water absorbed between paint specimens is fairly large and of the same order of magnitude as the variation caused by the presence of salt.

The results of the absorption isotherm experiments were used to calculate constants for a linearized equation of state relating water concentration, salt concentration, and external pressure. The equation of state appears in the mathematical and computer models as:

$$C_w = C_w^{\circ} + A_1 C_{\text{salt}} + A_2 (P - P_0) \quad (1)$$

where A_1 , A_2 , C_w° , and P_0 are constants, C_{salt} is the salt concentration, and P is the external pressure. For the small range of pressures expected in these systems, the external pressure was assumed to affect only the activity of components in the external solutions, i.e., the effect of the external pressure on the activity coefficients in the polymer phase was neglected. Inclusion of these effects and others are of course possible, but in view of the observed variability of the absorption isotherms between

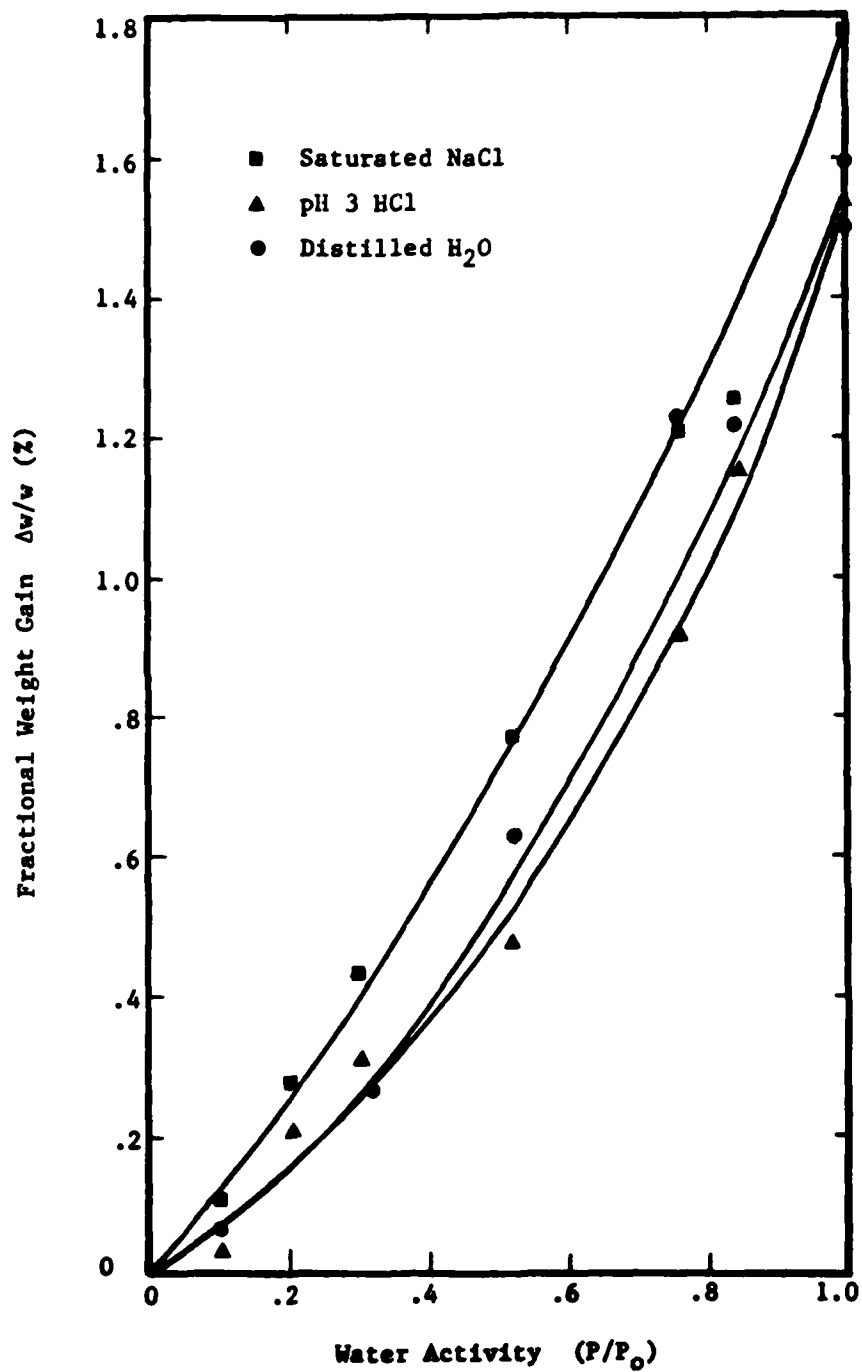


Figure 1. Absorption isotherm of water in polyurethane at 20°C.

test specimens, none of these refinements were deemed justified.

Water permeability

The permeability of water through polyurethane paint has been measured using diffusion cups (ASTM E96-66, procedure BW). In this experiment liquid water is placed in a glass vessel which is then sealed with a polyurethane membrane. The vessel is placed in a position such that liquid water always covers the membrane surface inside the vessel. The exterior membrane surface is maintained at zero water partial pressure by contacting with air dried by a dessicant and circulated with a fan. The temperature was maintained constant $\pm 2^{\circ}\text{C}$ by external heating coils. The weight of the diffusion cups was measured daily, and the results plotted as weight loss versus time as shown in Figure 2.

Figure 2 illustrates the results of a typical experiment conducted over a sixty-day period at constant temperature. The most striking feature of these results is that the permeability changes with time as indicated by the downward curve of weight loss versus time. This indicates that some change is taking place within the polyurethane membrane. If the diffusional process is not at steady state, the weight loss is expected to increase with time; the explanation appears to be that the membrane properties are changing with time. The particular membrane represented by Figure 2 was relatively fresh, about three weeks old at the beginning of the experiment, but similar behavior has been observed on six month old membranes. The experiments indicate that these polyurethane paint films age continually after being formed.

In addition to the experiments described above using distilled water on one side of the membrane, similar experiments were conducted with KCl solution in contact with the membrane. Various salt concentrations were used from 3.2×10^{-3} M to 3.2 M. The results are reported in Table I as reduced diffusion coefficient versus salt concentration. The reduced diffusion coefficient (D/D°) represents the diffusion coefficient for the cases where salt was used, normalized to that obtained for the same membrane and distilled water. Table I clearly indicates that the diffusion coefficient

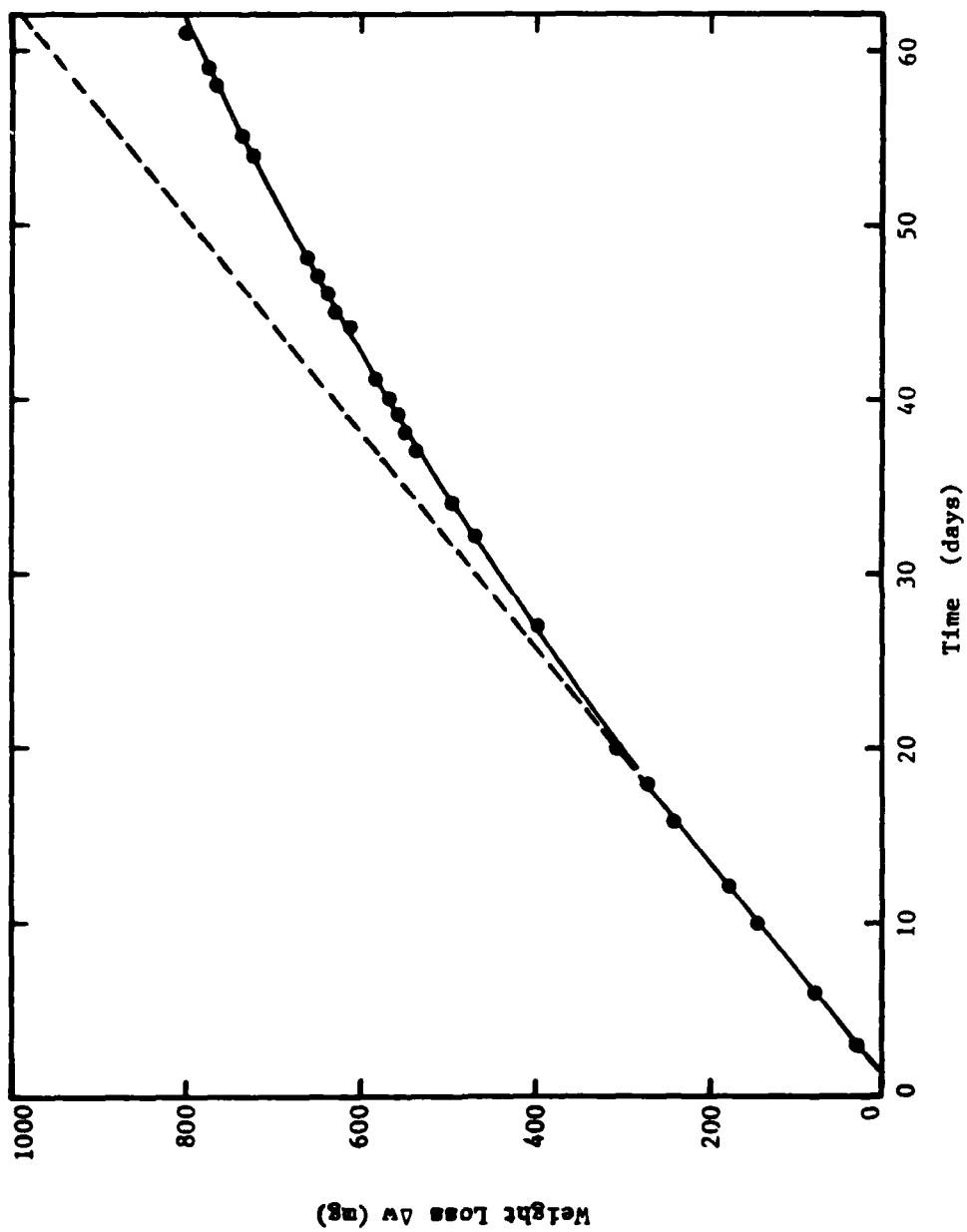


Figure 2. Water permeability through polyurethane.

Table I

Corrected D/D° Values

KCl (M)					
Concentration	0.00319	0.0319	0.100	0.319	3.195
<u>Sample No.</u>					
1					1.021
5				0.823	
1		1.026			
2			1.047		
5	1.032				
2				0.967	
5				0.956	

Table II

Permeability Coefficients (mg/cm·day) $\times 10^2$

Temp (°C)	24.88	30.75	41.34	24.52
<u>Membrane No.</u>				
1	2.133	3.541	7.128	2.570
2	1.868	2.663	5.938	2.087
3	2.255	3.469	8.641	2.047
4	1.765	2.912	7.384	2.083
5	1.852	3.554	7.347	2.035
Average	1.975	3.228	7.228	2.164

for water is unchanged even when high concentrations of salt are used. This is consistent with the view, discussed below, that ions enter the paint very slowly and to a small extent. The diffusion of water is thus affected primarily through the activity change of the external water resulting from the presence of salt.

Diffusion cup experiments have also been performed with polyurethane at various temperatures from 20°C to about 40°C. The results are illustrated in Table II as permeability (mg/cm·day) versus temperature. These results indicate that the permeability is a strong, increasing function of temperature; however, the only experimental determination of the water solubility was conducted at 21°C, thus precluding separation of the effect of temperature on solubility from that on diffusivity. Regardless of which factor, solubility or diffusivity, is most importantly responsible for the increasing permeability with rising temperature, it is clear that the diffusional properties of paint films are highly temperature dependent. This temperature dependence is consistent with other observations of the temperature dependence of physical and electrical properties for this type of polyurethane, and in fact, may be much more generally important to the performance of paint films than has been previously appreciated.

In addition to the diffusion cup experiments on water permeability, the permeation of tritiated (H^3) water was measured. The diffusion coefficients of water calculated from these experiments are reported in Table III. These results are similar to those obtained in the diffusion cup experiments. The range of values ($D_{\text{high}}/D_{\text{low}} = 3.7$) is similar to that found for other paints and is believed to represent the variation between similar samples of the same paint formed at different times (different ages) under slightly different conditions (curing temperature, relative humidity, etc.).

The good agreement between the water diffusivity obtained from diffusion cup and radiotracer experiments indicates that the diffusivity of water in polyurethane is relatively independent of water concentration. The average concentration in these two experiments varies by about a factor of two, but no change in diffusivity is observed. This behavior is expected only if the diffusivity is independent of concentration. The observed value

Table III
Radiotracer Determinations of
Water Diffusivity in Polyurethane

<u>Experiment</u>	<u>Diffusivity</u> <u>(cm²/s) x 10⁸</u>	<u>Temperature</u> <u>estimated ±3°C</u>
1	4.56	
2	4.56	23
3	3.28	24
4	1.23	28
5	3.84	24
6	4.06	26

for water diffusivity at 21°C is close to $3.2 \times 10^{-8} \text{ cm}^2/\text{s}$.

Ion Permeability

The permeability of sodium and chloride ions has been investigated in free films of polyurethane paint. In a first attempt to make these measurements, chloride specific electrodes were used and found to be insufficiently sensitive to determine the small changes in concentration due to the chloride flux across a paint film. Therefore, a more sensitive, radiotracer method was used to reduce the detection limit of ions; radioactive sodium-24 and chloride-36 were employed. Liquid scintillation was used to detect the beta decay rate of both tracer isotopes, but because both isotopic species have similar energy spectra, separate experiments were required for each tracer.

Three types of radiotracer experiments were performed: self-diffusion, dialysis, and Hittorf. In self-diffusion experiments the electrolyte (NaCl) concentrations on each side of the membrane were maintained constant and equal, and the fluxes of tritiated water, and ionic radiotracers were measured by extracting small (10 μl) samples of liquid for scintillation analysis. Dialysis experiments were similar to self-diffusion experiments except that an electrolyte concentration gradient was formed across the membrane, as opposed to a gradient in radioactive material only. The concentration gradient was formed in such a way as to enhance the net flux of chloride or sodium ions in the direction of the radioionic flux. The third type of experiment, Hittorf, adds an electric potential, as sensed by silver-silver chloride electrodes, across the membrane in such a manner as to increase the radioionic flux. Seven radiotracer experiments were successfully completed. No measurable flux of either sodium-24 or chloride-36 was detected in any of these experiments. These data have been used to establish an upper bound for both of the permeabilities involved; however, without further information about the solubility or diffusivity of the pertinent salt in polyurethane more quantitative analysis is not possible. Several methods have been attempted to establish one or the other of these two important parameters (solubility of NaCl or diffusivity of either Na^+

or Cl^-) with little success yet.

Hittorf Experiments

Hittorf experiments, as discussed above, involve the passage of current between two electrolyte solutions separated by a membrane. As charge is passed through the membrane, ions are transported from one compartment to the other, usually accompanied by a change in electrolyte concentration in the solutions adjacent to the membrane. These changes can be used to establish the ionic transference numbers. The flux of electrolyte is related to the current density (i) as follows:

$$N_{j\text{migr}} = \frac{i_j}{z_j F} t_j \quad (2)$$

where $N_{j\text{migr}}$ is the migration flux in the absence of concentration gradients, t_j is the transference number for the j^{th} ionic species, z_j is the ionic charge, and F is the Faraday constant. This equation can be integrated with respect to time; the resulting expression relates net electrolyte transport to total charge passed. Measurement of the change in salt concentration as a function of total charge passed is necessary to calculate transference numbers using the Hittorf method.

Four Hittorf experiments, two employing radiotracers, were conducted, but no measurable changes in electrolyte concentrations were found. This fact is consistent with the observation of exceedingly low conductivities for polyurethane ($\approx 2. \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$) in 0.1 M NaCl solution. As a consequence of the immeasurably small changes in electrolyte concentration, other means (discussed below) were employed to calculate transference numbers. Despite these problems, the Hittorf experiments produced important results: current versus voltage at various film thicknesses. These results were used to check the validity of the computer simulation of a free paint film.

Transference Numbers by Dialysis

When a membrane separates two electrolyte solutions of different activity, a potential is observed. For two identical sensing electrodes

reversible to negative ions when the concentration dependence of the transference number in the paint film can be ignored, the observed potential is related to the external salt activities by

$$U = E_1 - E_2 = -\left(\frac{v}{z-v_-}\right) \left(\frac{RT}{F}\right) t_+ \ln\left(\frac{A_{\pm 1}}{A_{\pm 2}}\right) \quad (3)$$

where v represents the total moles of ions per mole of salt, v_- is the moles of negative ions per mole of salt, and $A_{\pm 1}$ is the activity of salt on side one of the membrane. The slope of a potential versus natural logarithm of ionic activity plot, holding the concentration on side two of the membrane constant, is easily related to the cation transference number by

$$t_+ = -\frac{z-v_-}{v} \frac{F}{RT} \frac{dU}{d\ln A_{\pm 1}} \quad (4)$$

Figure 3 shows such a plot and illustrates the technique, and Table IV shows transference numbers, calculated from the straight line segments of these curves, as a function of concentration. Straight lines are obtained over about a three decade change in activity (concentration). The plots become nonlinear at low concentrations for two reasons: the transference number is no longer independent of concentration, and the silver-silver chloride sensing electrodes begin approaching their limiting concentrations. Of these two effects the first apparently becomes important at about 10^{-3} M NaCl. The solubility of silver chloride limits the useful range of silver-silver chloride electrodes to concentrations above about 10^{-4} M chloride.

Table IV

Sodium and Chloride Ion Transference Numbers at 21°C

Constant Concentration	Concentration Range	t_+	t_-
3M	3M - 10^{-2} M	0.358	0.642
1M	3M - 10^{-2} M	0.380	0.620
.1M	3M - 10^{-2} M	0.360	0.640
.01M	3M - 10^{-2} M	0.423	0.577

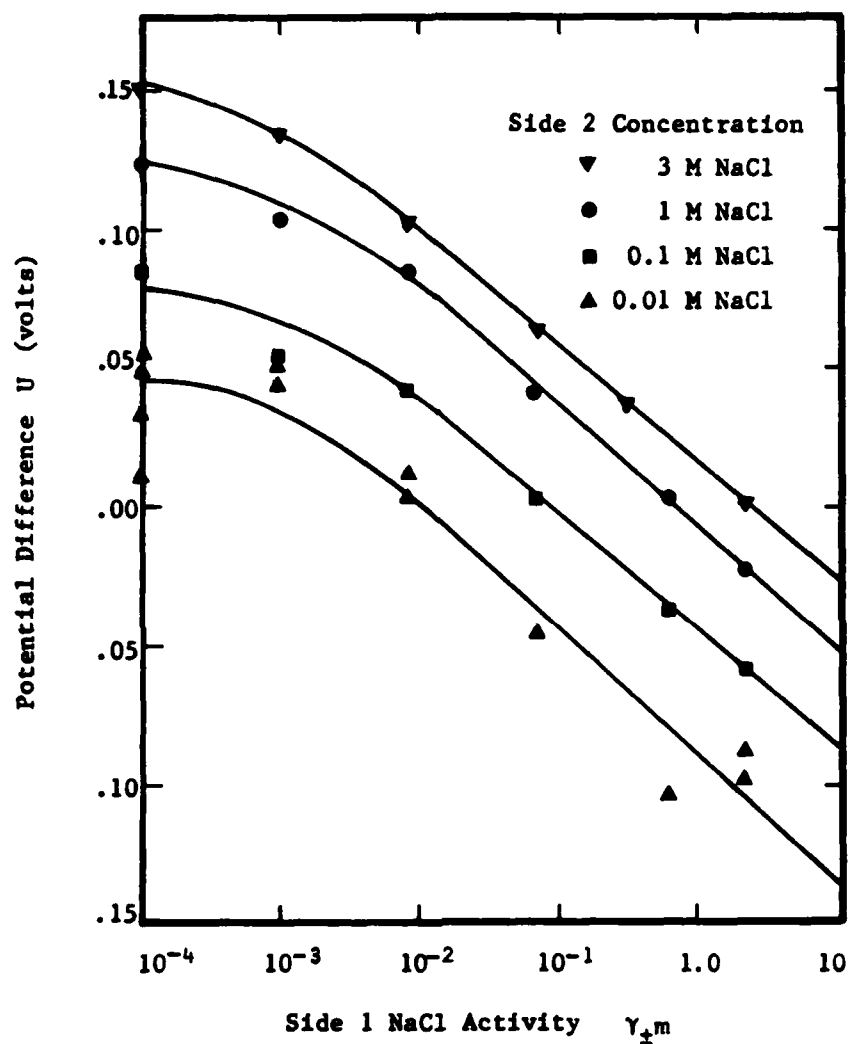


Figure 3. Potential difference across a polyurethane free film separating solutions of different concentration.

Consider the assumption that transference numbers are concentration independent. Several points can be made indicating that the observed nonlinear portions of the curves in Figure 3 are to be expected. First, the polyurethane membranes have anion transference numbers (t_-) greater than 0.5. This is probably the result of chemically bound positive charges within the membrane. In this case, the anion transference number is expected to approach the value one in the limit of infinitely-dilute external solution. Equation 3 indicates that in this situation ($t_+ = 1 - t_- = 0$) the observed potential will be zero volts. The second point is brought out by considering why the concentration dependence becomes important at low concentrations. Although the exact concentration of fixed charge within the membrane is unknown, the magnitude is very low ($< 5 \times 10^{-6}$ mole/cm³). Thus, relatively-low external solution concentrations might be considered concentrated. Under these conditions the concentration of positive and negative ions inside the paint will be nearly equal. The transference number can be expressed:

$$t_+ = \frac{z_+^2 D_+ C_+}{z_+^2 D_+ C_+ + z_-^2 D_- C_-} \quad (5)$$

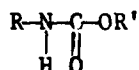
and for equal cation and anion concentrations

$$t_+ = \frac{z_+^2 D_+}{z_+^2 D_+ + z_-^2 D_-} \quad (6)$$

where D_+ is the diffusivity of positive ions, C_+ is the concentration of positive ions, and similarly for negative ions. Equation 6 indicates that for concentration-independent diffusivities, the transference number will be constant. One can thereby conclude that in highly-concentrated external electrolyte the transference number will be constant and the membrane potential will be a linear function of the logarithm of ionic activity; however, as the external concentration decreases the potential will eventually be forced to zero as the cation concentration and transference number within the membrane approaches zero (equation 4). The computerized model of polyurethane has also predicted this type of potential fall-off.

Ionic Capacity

As discussed above, the polyurethane films have been assumed to possess fixed ionic charge. The urethane linkage has the form



which could have some weak ionic capacity. As a first approximation, the model allows for only a single type fixed charge. The fixed charge valence is unknown, and has been arbitrarily set at ± 1 . Transference number data indicate that the fixed charge in polyurethane carries a positive sign, but the concentration of charged sites within the membrane (C_m) remains undetermined.

Several attempts have been made to establish the ionic capacitance (C_m) of these paint films. The first attempt involved titration. The membrane was soaked in concentrated sodium hydroxide (pH = 12 or 13) for several days and was then placed in dilute acid (HCl) solution. The chloride ions were expected to replace the hydroxyl ions within the membrane, and the extent of this exchange could be followed as the pH of the acid solution. Several problems were encountered; fairly large pieces of thin paint (large surface area) were needed in a small acid volume. This created problems in pH measurement and sample handling; however, it soon became apparent that the primary problem was the low magnitude of the ionic capacitance. As a result of this low ionic capacity, carbon dioxide interfered with pH measurements, and the ionic capacitance of glassware became important. Because of these difficulties, no accurate determinations of ionic capacitance were obtained using titration methods.

A second attempt employing radioactive isotopes was then investigated. A solution containing tritiated (H^3) water, sodium (Na^{24}), and chloride (Cl^{36}) was used. A small piece of paint (≈ 40 mg) was placed in the cavity formed between two pieces of Plexiglas by a doughnut shaped gasket. The paint was allowed to exchange ions when the cavity was filled with the solution containing radiotracers. A liquid scintillation counter was used to determine the tritium content of the paint. This determination, in the presence of sodium and chloride, is possible because the average beta

energy of tritium is much lower than that of either of the other isotopes. We were thus able to determine the solubility of water in polyurethane under experimental conditions. This solubility was compared to that measured by gravimetric methods (Absorption of Water section), as a check on the experimental technique, and good agreement was obtained. Determination, by liquid scintillation counting alone, of the two remaining activities was precluded by the similar energy spectra of chloride and sodium. However, sodium can be determined independently by coincidence counting the gamma emission. When this method was used, no interference was noted from the chloride. Once the gamma count had revealed the sodium content of the paint, a liquid scintillation count representing the sum of chloride and sodium present could be used to calculate the chloride content of the paint. This method has been attempted and has proved to be partially successful.

The first effort to measure ionic capacitance using radioisotopes failed because the gasket material (a common rubber) had a much higher ionic capacitance than the paint film. A second effort using a Teflon gasket also failed because the cell leaked and dried out after several days. Finally the same Teflon gasket was employed, but a thin film of silicone stopcock grease was used to seal the edges. This procedure produced quite satisfactory results, and a single test was completed after soaking the paint for two weeks.

Using the liquid scintillation and coincidence gamma counting techniques, discussed above, the chloride and sodium contents of the paint were determined. The ionic capacitance was assumed to be equal to the positive difference between these concentrations. This assumption is based on the electroneutrality condition:

$$-z_m C_m = z_+ C_+ + z_- C_- \quad (7)$$

where z is the valence and C is the concentration of the particular species in question (sodium or chloride ions, or membrane fixed charge). For our situation, Equation 7 reduces to:

$$-z_m C_m = C_+ - C_- \quad (8)$$

The experimental results are indicated in Table V below.

Table V
Results of Ionic Capacitance Experiment
Using Radiotracers

Species	C_+	C_-	$z_m C_m$
concentration (mole/g-paint)	1.6×10^{-8}	4.6×10^{-6}	4.6×10^{-6}

These results at first appear very encouraging; the ionic capacitance is lower than the values reported elsewhere (2-5) but not unreasonably so. A problem is encountered, however, when employing this value of the ionic capacitance in the mathematical model. The model indicates that in order for an ionic capacitance of this magnitude to be compatible with the other observations, conductivity versus external concentration, and potential versus external concentration difference, for example, the diffusion coefficients for ions must be exceedingly low; in the neighborhood of 10^{-12} cm²/s. Although diffusion coefficients of this magnitude may exist (6), if this is true, the paint film would not have reached thermodynamic equilibrium in the two-week duration of the experiment. Thus the calculated value of C_m will probably be in error.

The effects of nonequilibrium can be investigated by considering that because the membrane possesses positive fixed charge, the negative chloride ions are expected to move through the paint more easily than sodium. In the non-steady state, the paint might then contain an excess of chloride ions and the ionic capacity appear too high. This thought is further supported by the fact that the salt concentration of the solution in contact with the paint was 0.09 M NaCl. Conductivity data indicate that this is a concentrated solution as far as the membrane is concerned. This means that at equilibrium the concentrations of all mobile ions in the paint are expected to be much greater than the ionic capacitance. This is inconsistent with the experimental results (Table V) and indicates that a non-steady state condition exists inside the paint even after two weeks.

Reverse Osmosis Tests

Reverse osmosis tests were conducted to determine the Darcy's Law constant (α) for paint films. In general a pressure gradient can be expected across paint films in the field. Furthermore, the equation of state (Equation 1) indicates that inside the paint film one can expect pressure, as well as concentration, and potential gradients. The constant, α , relates the water flow to the observed pressure gradient.

The reverse osmosis experiments were conducted at UCLA under the direction of Prof. D.N. Bennion. The apparatus and experimental technique are discussed elsewhere (7, 8). Two experiments, at pressure differences of 225 psi and 700 psi, were performed with the result that no measurable flow was observed. From this information an upper limit for the Darcy's Law constant was calculated:

$$\alpha_{\max} = 7.9 \times 10^{-20} \frac{\text{m}^4}{\text{N} \cdot \text{s}} \quad (9)$$

For values of alpha in this range, the computer model proved to be very insensitive to the value of alpha. Best results were obtained for a value of

$$\alpha = 0.5 \times 10^{-20} \frac{\text{m}^4}{\text{N} \cdot \text{s}} \quad (10)$$

6.3 Mathematical and Computer Modeling

A mathematical model has been developed to quantitatively describe the transport across paint films (1). A computer program has been written to solve the differential equations of the mathematical model. The program calculates the fluxes of all mobile species, as well as the potential, for a given current density. The concentrations or fluxes of all species must be specified at the paint surfaces. For the experiments described above, Hittorf, dialysis, self-diffusion, and reverse osmosis, there is a total of three mobile species: sodium ions, chloride ions, and water. In all of these experiments a paint membrane separates two aqueous solutions. Under these conditions the concentrations in the paint at each paint-solution interface

will be specified by chemical equilibrium with the external solutions.

The relation between the concentration of ions in solution to that in the paint has been assumed to be accurately described by Donnan equilibrium:

$$C_+ = \frac{C_m}{2} \left[-\frac{z_m}{z_+} + \sqrt{\left(\frac{z_m}{z_+}\right)^2 + 4 K_{\pm} \left(\frac{C}{C_m}\right)^2} \right] \quad (11)$$

where C_+ is the concentration of cations in the paint, C_m is the ionic capacitance, C is the salt concentration in bulk solution, and $K_{\pm}$ is the equilibrium distribution coefficient for salt between the paint and the bulk solution:

$$K_{\pm} = \frac{C_+^{v_+} C_-^{v_-}}{C^v} \quad (12)$$

where $v = v_+ + v_-$ represents the total moles of ions per mole of salt, and other terms have been previously defined. Thus, once $K_{\pm}$ is known, the ion concentration in the paint, at the solution interface, is specified by the external electrolyte concentration.

After the ion concentration at the paint-solution interface has been specified, one independent variable remains; either pressure or water concentration may be chosen. The value of the last variable is fixed through the equation of state. Thus by knowing the pressure and bulk solution concentrations, the conditions in the paint at the paint-solution interfaces are specified, as required by the model.

Throughout the preceding discussion it has been assumed that no boundary layer exists in the aqueous phase. This position is supported by the fact that the only flux of measurable magnitude is that of water. Also, the potential drop in solution has been measured with a mobile reference electrode and been found to be negligible. Furthermore, the solutions have been vigorously stirred using Teflon coated magnets throughout the course of all experiments. All indications are that the assumption is good.

The data obtained from eight Hittorf, dialysis, and self-diffusion experiments were reproduced, within $\pm 50\%$, by the computer simulated paint film. It is expected that much more accurate simulations can be obtained, but, for reasons discussed below, no attempt was made to achieve higher precision at this time. In addition to these data, the general nature of the transference number and conductivity versus concentration experiments were predicted; however, some difficulty was encountered in modeling the fall-off of conductivity versus concentration in the region near the knee in the curve (Figure 4). The counterion concentration and the conductivity become constant at low electrolyte concentrations (the concentration of sodium ions approaches zero in this limiting condition). At high electrolyte concentrations, the model predicts an increasing conductivity with increasing concentration. Both these regions can be accurately modeled, but the region in between is modeled only approximately. This fact taken alone is not particularly serious; however, the parameters which best model the conductivity versus concentration curve do not produce a particularly good fit to the series of eight Hittorf, etc., experiments. This situation arises primarily because no reliable value of the ionic capacitance is yet available.

As described above (see ionic capacity) indications are that an incorrect value of C_m has been obtained from experiments. Therefore, a test of the computer model was undertaken to examine whether different values of C_m would yield acceptable results for only the eight Hittorf, etc., experiments. The test clearly demonstrated that for values $10^{-3} < C_m < 1 \text{ mole/m}^3$ substantial agreement between experimental data and the computer model can be achieved. Since the model is capable of fitting the group of eight experiments in one region of "coefficient space" and the conductivity versus concentration curve in another region, it seems likely that a region will be found in which all experimental observations can be satisfactorily modeled.

Although the model has not accurately described all the observed paint film behavior at this time, it is highly unlikely that any model not accurately representing the primary features of transport through a polymer film could describe, with a single set of coefficients, the various

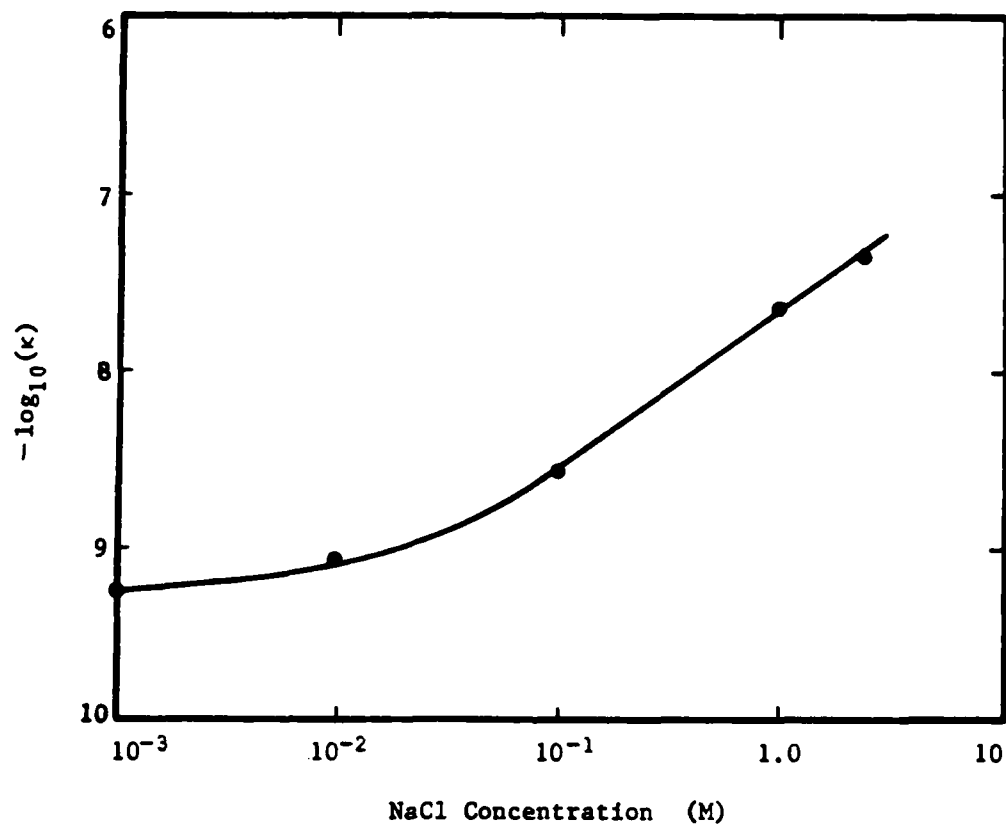


Figure 4. Polyurethane conductivity (dc) versus concentration in sodium chloride solution.
Thickness = 8.3×10^{-3} cm. $\kappa [=] \Omega^{-1}\text{m}^{-1}$.

behavior exhibited by the series of eight experiments (Hittorf, etc.). The model also predicts the correct general behavior observed in the transference and conductivity versus concentration experiments. It is thus expected that if supplied with a correct set of parameters, in particular C_m and ionic diffusion coefficients, the model will accurately predict all the observations related to transport through polyurethane.

Despite the difficulties discussed above, several conclusions can be drawn concerning the transport properties of polyurethane paint. Although the ionic capacity remains unknown, it is quite low, probably

$$C_m < 5 \times 10^{-6} \text{ mole/cm}^3 \quad (13)$$

The net fixed charge in the paint is positive. The Darcy's Law constant (α) has an approximate value of

$$\alpha \cong 5 \times 10^{-21} \frac{\text{m}^4}{\text{N} \cdot \text{s}} \quad (14)$$

The diffusion coefficients for ions are not well known but they are certainly less than $10^{-8} \text{ cm}^2/\text{s}$ and probably less than $10^{-10} \text{ cm}^2/\text{s}$. The solubility of water is quite well known,

$$C_{\text{sat}} = 0.013 \text{ g-water/g-paint} \quad (15)$$

The diffusivity of water is also quite well established:

$$D_{\text{H}_2\text{O}} = 3.2 \times 10^{-8} \text{ cm}^2/\text{s at } 21^\circ\text{C} \quad (16)$$

Also, the water diffusion appears to be independent of the current density and nearly independent of salt concentration in the paint. Thus, in many respects the paint membrane can be considered to be an ideal semi-permeable membrane; allowing water to pass while remaining impermeable to ions.

Consideration of the evidence presented above produces two conclusions:

- (1) The transport of ions through polyurethane is very low, perhaps negligible,
- (2) Water (and probably oxygen) is transported much faster according to its activity gradient.

This means that water penetrates the paint quickly and is near unit activity at the metal interface after a very short exposure time (≈ 30 min). This picture also indicates that ions trapped under the paint on the metal surface are exceedingly important in the corrosion process. This conclusion is consistent with the fact that surface preparation of samples is known to affect test results.

It is interesting to consider also the model predictions, if ion transport through the paint film can be neglected. Then the value of ionic capacitance used in the transport model becomes much less crucial, especially since almost all solutions encountered in the field can be considered concentrated ($C_{\text{salt}} > 10^{-2}$ M); therefore, there is no need for the model to fit the transition data in the region between concentrated and dilute solutions, i.e., the knee region of the conductivity versus concentration curve. The model can thus be expected to yield good quantitative results in this case.

6.4 Filiform Corrosion

During the experimental work, several instances of filiform corrosion were observed. Also, several literature references were encountered discussing filiform corrosion. Filiform corrosion occurs at the paint-metal interface and is produced as an active (wet) head travels across the metal at the paint-metal interface. The track, or tail, behind the active head is dry and filled with corrosion products (Fe_2O_3 on iron). All the theories presented in the papers discussing this phenomenon considered filiform to be some kind of oxygen driven corrosion cell involving the diffusional transport of oxygen and water through the paint. This thought appeared to be contrary to the experimentally observed fact that filiform corrosion is relatively independent of paint type and should be independent of diffusion through the paint. Further consideration of published observations led to the conclusion that the primary pathway through which oxygen and water reach the actively corroding head region is a porous tail. Previously, authors studying filiform corrosion had overlooked this diffusion pathway. A brief review of the reasoning which led to the proposal of this new filiform mechanism is given in appendix A. This

work was presented at the Fall 1979 meeting of The Electrochemical Society (9).

Once the feasibility of oxygen diffusion through a porous tail had been firmly established, experiments were conducted to test the hypothesis. These experiments involved polyurethane paint on iron test samples. Filiform corrosion was initiated by breaking the paint at a point and doping the break with a few microliters of concentrated sodium chloride solution. These samples were then placed in a controlled atmosphere and maintained at about 90% relative humidity and room temperature ($\approx 21^{\circ}\text{C}$). Under these conditions, filiform tracks grew freely, and positions of the heads were periodically recorded (Figures 5-7). After the corrosion was actively progressing, several of the filiform tracks were cut across the tail with a scalpel. The paint on the side of the cut away from the head was peeled back, and the filiform tail was plugged with epoxy glue. As reference experiments, several tails were not cut, but were covered with epoxy, and several others were cut through but not epoxied. After about two weeks time in the humidity chamber, the progress of the filiforms was compared. The filiform tracks for which the tails had been both cut and epoxied had stopped (Figures 5-6), whereas all the others had continued to travel at a normal pace. When the stopped tracks were again opened to a source of oxygen, either by cutting with a scalpel or by intercepting the path of a growing filiform, the corrosion continued as though the tail were unblocked (Figure 7). These experiments have been repeated many times and lend strong support to the contention that oxygen and water reach the actively corroding head region by diffusing through the porous tail.

The hypothesis of a porous filiform tail is consistent with other observations. It explains, for example, the front-back nature of filiform. Oxygen is present at the back of the head at higher activity than at the front. This produces a separation of anodic and cathodic sites and explains why the pH at the front edge of the head is low (≈ 2) and that at the rear much higher (4 to 8) (10, 11). It explains why filiform tracks do not cross each other, preferring to stop or change direction away, when a head encounters a filiform tail. Obviously in such situations a

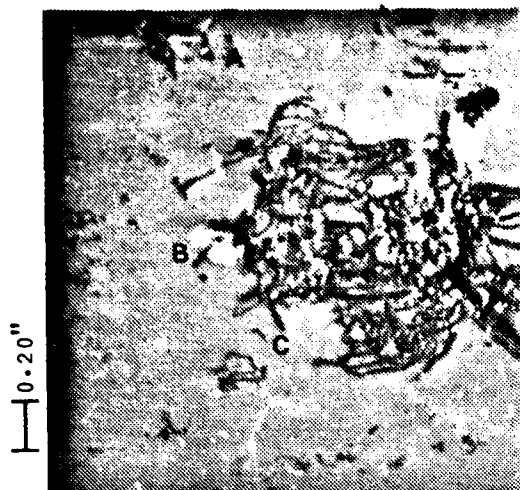


Figure 5. Filiform tracks under polyurethane on iron, July 23, 1979.

Track A cut and epoxied.
Track B cut and epoxied.
Track C unaltered.

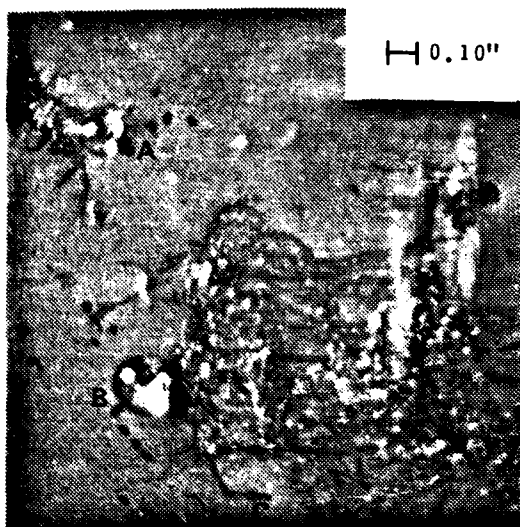


Figure 6. Filiform tracks under polyurethane on iron, July 31, 1979. Same experiment as Figure 5.

Track A cut and epoxied on July 23, 1979.
Track B cut and epoxied on July 23, 1979.
Track C unaltered.

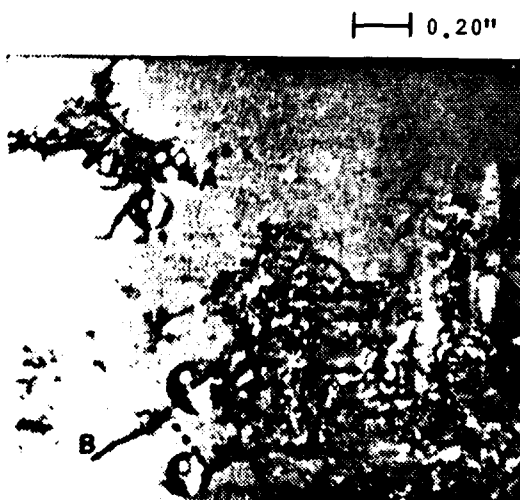


Figure 7. Filiform tracks under polyurethane on iron, August 20, 1979. Same experiment as Figures 5 and 6.

Track A cut and epoxied on July 23, 1979.
Track B cut open on July 31, 1979.
Track C unaltered.

new cathodic (oxygen rich) region is formed and the relative positions of anode and cathode are changed. The hypothesis is also consistent with the critical relative humidity limits observed for filiform corrosion; if the humidity is too high, water condenses in the tail and blocks oxygen diffusion, and if too low, the head dries and corrosion stops. These, as well as other observations of this phenomenon discussed in the literature, are strong evidence that the new hypothesis is correct.

6.5 Resistance Capacitance Oscillations

As a consequence of the fact that paint is known to acquire water and mobile ions when immersed in aqueous electrolyte solutions it was thought that these changes might be easily monitored employing electrical methods. To this end capacitance testing equipment was used to measure the equivalent series resistance and capacitance of free paint films and painted metal samples. Although these methods have not proved particularly useful for predicting corrosion properties of paints, they produced some very interesting observations which will now be discussed.

Electrolyte penetration theories indicate that as time passes, paint film resistance must fall and capacitance should increase. These theories contain no mechanism which can explain an increasing resistance with time; however, that is precisely what was observed with polyurethane free films and painted zinc specimens placed in aqueous electrolyte (NaCl). Furthermore, these tests revealed a rather steady oscillation in both resistance and capacitance having a period of thirty to forty-five minutes. An example is shown in Figure 8. The resistance changed a factor of two to three during these oscillations, and each resistance change was accompanied by a capacitance change in the opposite direction. This phenomenon was eventually linked to a temperature gradient across the paint film. Temperature differences of less than 0.5°C were shown to trigger the oscillations.

Although a study to determine the mechanism governing this oscillatory behavior was not undertaken, similar behavior has been observed for other systems (12, 13). The primary feature of theories presented in these studies

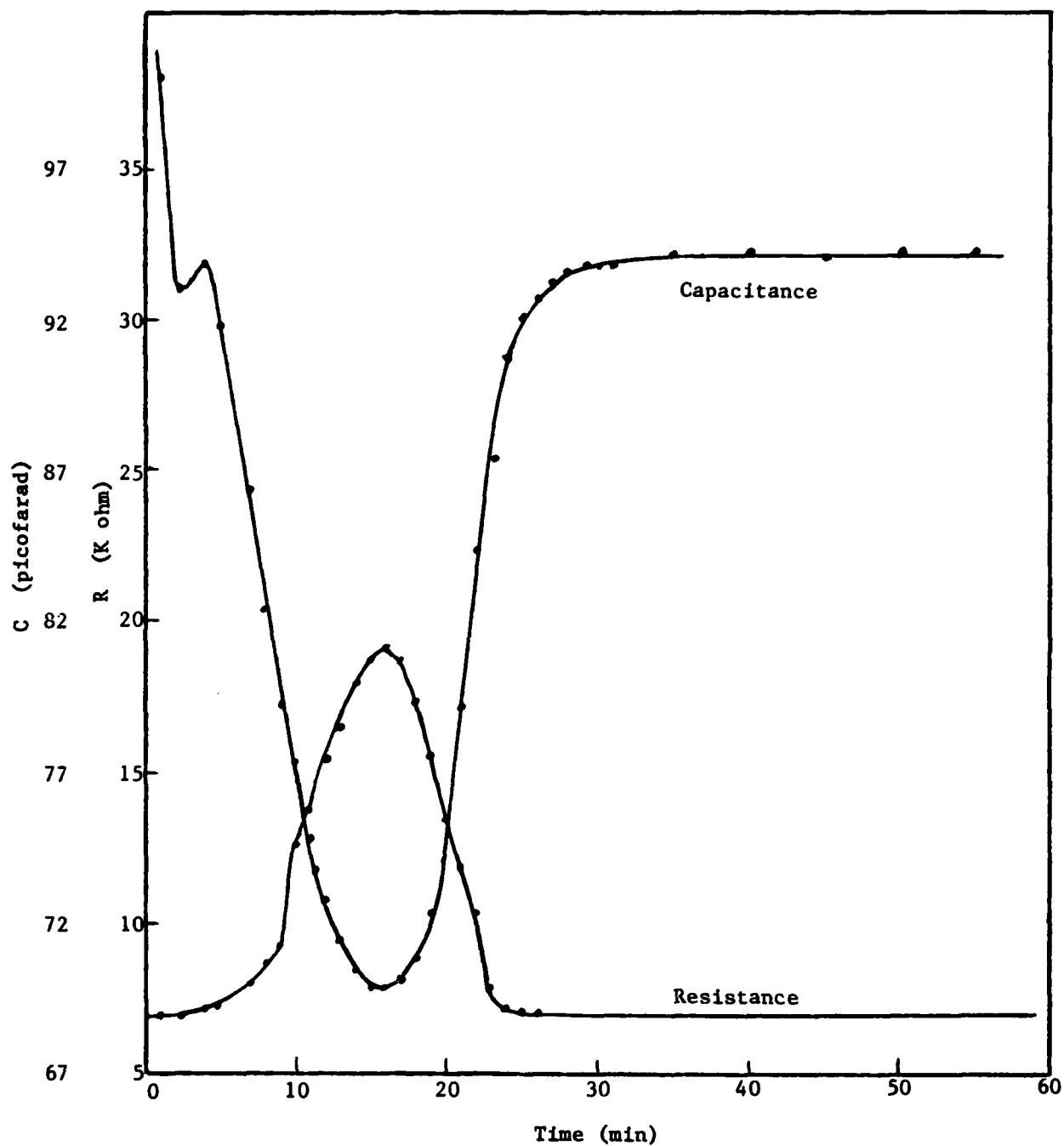


Figure 8. Initial change in resistance and capacitance of 1.0 mil polyurethane film on zinc exposed to 0.5 M NaCl at 21 C.

involves a nonlinear dependence between the important variables. For instance, the diffusivity may be a nonlinear function of the concentration, or the conductivity a nonlinear function of the temperature, etc. Under such conditions, unstable behavior can be predicted for certain combinations of parameter values. Similar types of instability are known to exist in chemical reactors. Thus, although the detailed mechanisms are unknown for membranes in aqueous solutions, the general feature of oscillations is expected where nonlinear parameter relationships are present.

This conclusion is consistent with the fact that dynamic mechanical measurements of the rheological properties of polyurethane indicate highly nonlinear behavior of the elastic loss modulus (E'') near 20°C, as illustrated in Figure 9. (This curve was obtained at the University of Washington in the laboratory of Prof. Seferis in connection with another contract*.) Furthermore, Bell (14) has indicated that the diffusivity of a dye through a polymer can be expressed as follows:

$$\frac{D}{RT} = AE^{nB} \quad (17)$$

where A and B are constants. Although a dye molecule is considerably different from the mobile ions being considered here, this type of expression is widely used to describe diffusion in polymers. Equation 17 clearly indicates a nonlinear dependence of diffusivity on temperature for any system which exhibits a changing loss modulus. Another nonlinearity observed for polyurethane occurred in high-voltage conductivity experiments, where the current appeared to fit an equation of the form

$$i = A \sinh(B \cdot v) \quad (18)$$

and A and B are constants. This functional form of the current density dependence on voltage is known to be associated with activated diffusion (15), and in such cases the diffusivity will be an exponentially increasing function of the temperature. It thus appears highly likely that the observed oscillations of resistance and capacitance in polyurethane are related to a nonlinear dependence of diffusivity on temperature.

*ONR Contract No. N00014-79-C-0021

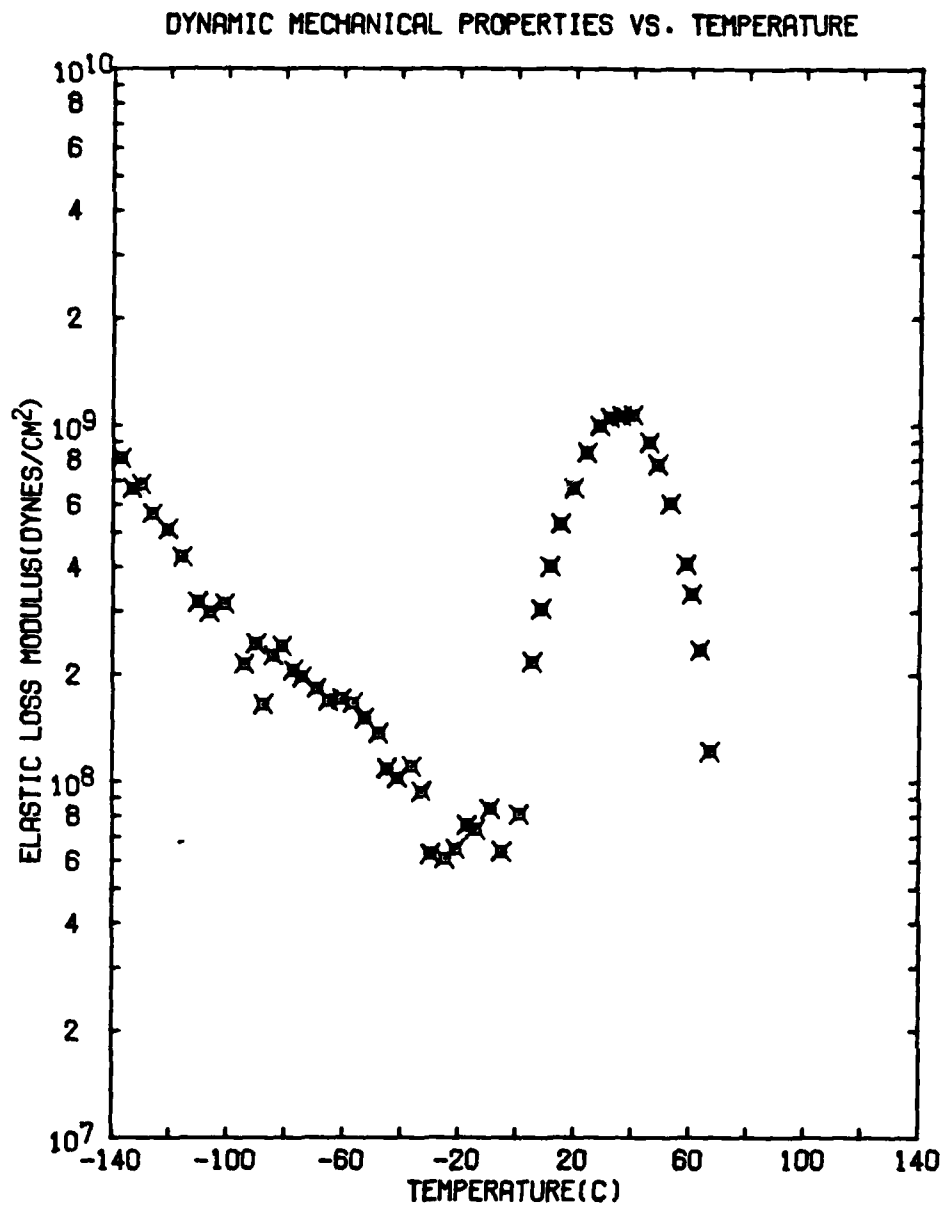


Figure 9. Polyurethane elastic loss modulus versus temperature.

6.6 Analysis of Corrosion Blisters

A set of experiments has been conducted in which the contents of corrosion blisters were analyzed. All combinations of polyurethane and epoxy paints with 2024 and 7075 aluminum were tested. The painted specimens were exposed to aqueous sodium chloride solutions for various time intervals. At the conclusion of the experiments, a sample of the external electrolyte was taken for determination of the salt concentration. Then the test coupon was removed from the electrolyte and dried. The corrosion blister was cut open, and whenever possible an interior liquid sample was taken. The solids from within the blister were also tested, although no accurate weights were obtained for these. Atomic adsorption spectroscopy was used to analyze all samples. The results indicate that very small amounts of ionic species are transferred through the paint films. The blister contents of a polyurethane-painted pure zinc sample were also analyzed and found to be primarily a concentrated solution of ZnCl_2 . This is consistent with the results for aluminum in which the primary component was an aluminum compound, probably $\text{Al}(\text{OH})_3$ or oxychloride. The external electrolyte in all cases was sodium chloride (0.15 M) solution, and although sodium was present inside the blisters, it was always a minor component (mole fraction <0.03). These data indicate that there may be two stages involved in the corrosion process. In the first stage, the solvent (H_2O) must pass through the paint in order for corrosion to proceed. Ions will either diffuse through the paint or they may have been covered by paint during application. In this initial phase, ion mobility is low and anodic and cathodic sites are in close proximity. In the second stage, after blisters have formed, the trapped electrolyte inside the solution constitutes a low resistance phase in contact with the metal. This allows separation of the anodic and cathodic reaction sites, and a conventional concentration driven corrosion cell can form in which the rate limiting step becomes either the diffusion of oxygen or water through the paint. Mayne (16, 17) has indicated that both these species diffuse through paint much faster than ions. This mechanism is supported further by the observation of very slow filiform corrosion of painted metals under submerged conditions during the program.

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Presented paper, "Conservation of Energy in the Electrochemical Process Industries," by T. R. Beck, N. P. Yao, and A. R. Landgrebe. The Electrochemical Society, Las Vegas Meeting, October 17-22, 1976.

Coauthored paper, "The Occurrence of Salt Films During Initial Stages of Corrosion," R. C. Alkire, D. Ernsberger, and T. R. Beck, presented at The Electrochemical Society Las Vegas Meeting, October 17-22, 1976.

Participated in ONR/NRL meeting on new directions in electrochemistry, ONR, Arlington, Va., October 28, 1976.

Presented seminar, "Surface Stress and Electrocapillary Curves for Solid Metals," Department of Chemistry, University of Washington, November 3, 1976.

Presented paper, "Industrial Electrochemistry--Past, Present and Future," to Pacific Northwest Section, The Electrochemical Society, Vancouver, B.C., April 30, 1977.

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Participated in ERDA Materials Sciences Overview, Workshop, Thermodynamics and Electrochemistry, Argonne National Labs, May 18-20, 1977.

Participated in AFOSR/AFML Corrosion Workshop, St. Augustine, FL, September 13-15, 1977.

Appointed Chairman, Electrolytic Technology Advisory Committee (Ad Hoc), for Department of Energy.

Abstracts submitted:

"Model for Protection by Paint Films," T. R. Beck and R. T. Ruggeri, to AIME Symposium on Corrosion Prevention and Control in Military Applications, Denver, February 26 to March 2, 1978.

"A Model for Mass Transport in Paint Films," R. T. Ruggeri and T. R. Beck, for the Electrochemical Society, Seattle, May 21-26, 1978.

Presented paper, "Passivation of New Titanium Surfaces," 4th International Symposium on Passivity, The Electrochemical Society, Airlie, VA, October 21, 1977.

"The Hows and Whys of Corrosion," presentation to Portland, OR section of NACE Corrosion Short Course, November 16, 1977.

Chaired meeting of Electrolytic Technology Advisory Committee (Ad Hoc), Denver, CO, March 2-3, 1978.

Presented paper, "Model for Protection by Paint Films," T. R. Beck and R. T. Ruggeri to AIIME Meeting on Corrosion Prevention and Control in Military Applications, Denver, CO, March 2, 1978.

R. T. Ruggeri presented his Ph.D. Thesis on March 14, 1978, Department of Chemical Engineering, University of Washington. Degree awarded June 1978.

Presented paper, "Surface Active Agents for Controlling Streaming Current Corrosion of Airplane Hydraulic Servo Control Valves," to Pacific Northwest Section, The Electrochemical Society, Inc., Vancouver, B.C., April 1, 1978.

Elected Chairman, Division VII, Electrochemical Engineering, International Society of Electrochemistry.

Served as outside reviewer to Argonne National Laboratories, Lithium/Metal Sulfide Battery Program, May 9-10, Argonne National Laboratories.

Host Chairman, 153rd Meeting, The Electrochemical Society, Inc., Seattle, WA, May 21-26, 1978.

R. T. Ruggeri presented paper, "A Model for Mass Transport in Paint Films," R. T. Ruggeri and T. R. Beck, The Electrochemical Society, Inc., Seattle, WA, May 22, 1978.

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Presented Keynote Lecture, "Energy Efficiency of Industrial Electrochemical Processes," to Division VII, 29th Meeting, International Society of Electrochemistry, Budapest, Hungary, August 29, 1978.

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Appendix

Mass Transport Analysis of Filiform Corrosion

R. T. Ruggeri and T. R. Beck

Presented to The Electrochemical Society, Los Angeles,

October 14-19, 1979, Extended Abstract No. 245

In order to develop an overall mechanism for filiform corrosion, it is necessary to review and condense data collected by different authors. Table I represents data from several sources and is typical of that found in the literature.

Table I
Filiform Corrosion of Iron

<u>Velocity</u>	<u>Width</u>	<u>Depth (metal)</u>	<u>Ref</u>
6×10^{-7} cm/s	0.015 cm	$5 \times 10^{-4} - 10^{-3}$ cm	1
	0.05 cm		2
2.3×10^{-7} cm/s	0.01 - 0.02 cm		3

From these data it is possible to establish the moles of iron corroded:

$$N = \frac{v \cdot w \cdot d \cdot \rho}{W} \quad (1)$$

where N = moles of iron corroded per second

v = velocity of filiform head

w = width of filament

d = depth of the track

ρ = density of iron

and W = molecular weight of iron

Substituting conservative values from Table I into equation 1 yields:

$$N_{Fe} = \frac{(2 \times 10^{-7} \text{ cm/s}) (0.01 \text{ cm}) (5 \times 10^{-4} \text{ cm}) (7.86 \text{ g/cm}^3)}{55.85 \text{ g/mole}} \quad (2)$$

$$N_{\text{Fe}} = 1.41 \times 10^{-13} \text{ mole-Fe/s} \quad (3)$$

$$I = (3 \text{ eq/mole})(96500 \text{ C/eq})(1.41 \times 10^{-13} \text{ mole/s}) \quad (4)$$

$$I = 4.07 \times 10^{-8} \text{ A} \quad (5)$$

Filiform corrosion has been shown to be independent of the particular paint used (4, 5), however, for the purposes of elucidation, certain assumptions will be made. First, certain geometrical conditions will be assumed:

(1) The filiform head has a circular contact interline with the metal, and (2) the paint is 5×10^{-3} cm thick. If we further assume that the filiform tail is a half cylinder, subsequent calculations will be simplified. These geometric conditions are represented in Figure 1.

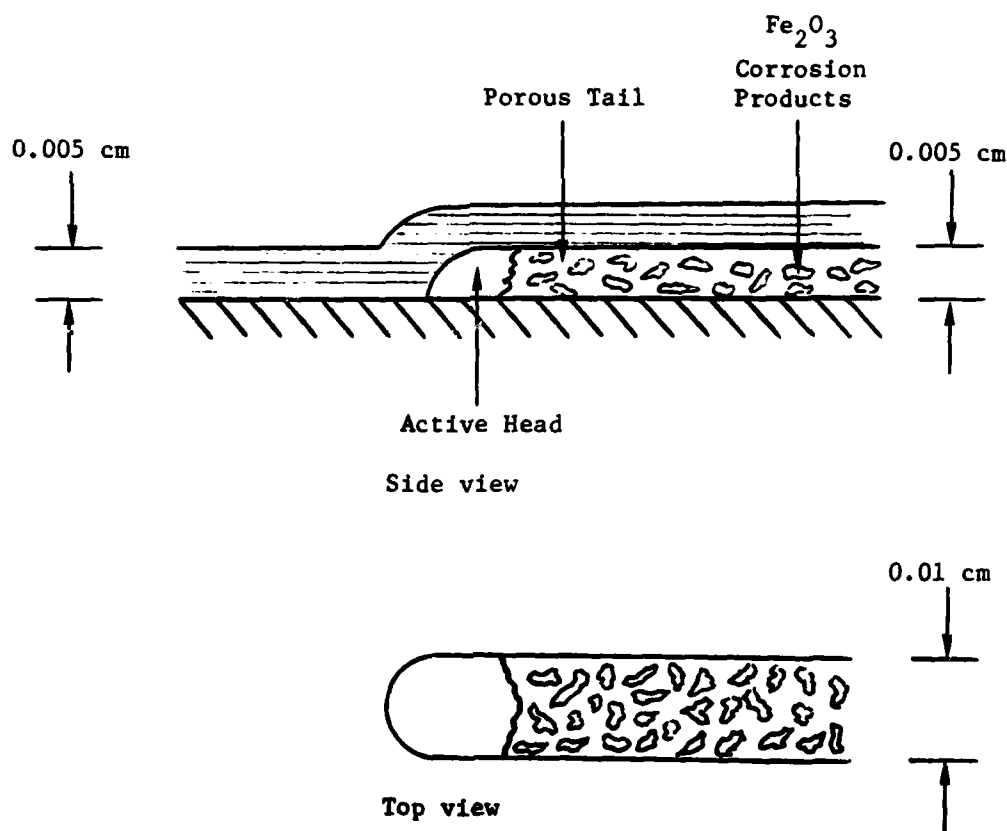


Figure 1. Schematic representation of a filiform corrosion cell.

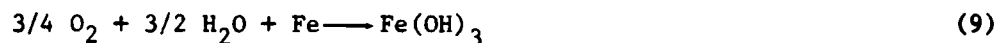
It has been proposed that the metal surface surrounding the filiform head supports the cathodic reaction.



The anodic reactions can be summarized as follows:



The total corrosion reaction is then the sum of reactions 6, 7, and 8



It has been stated that the cathodic area is about 100 times the area of the active head (4). A conservative estimate of the diffusion coefficient of O_2 through paint is:

$$D_{\text{O}_2} = 10^{-6} \text{ cm}^2/\text{s} \quad (10)$$

Taking the concentration of O_2 in air as

$$C_{\text{O}_2} = \frac{n}{V} = \frac{P}{RT} = 0.21 \text{ atm} / (0.082 \text{ l atm/mole } ^\circ\text{K}) \text{ } 298^\circ\text{K} \quad (11)$$

$$C_{\text{O}_2} = 8.6 \times 10^{-3} \text{ mole/l} \quad (12)$$

$$J_{\text{max}} = (10^{-6} \text{ cm}^2/\text{s}) (8.6 \times 10^{-3} \text{ mole/l}) (10^{-3} \text{ l/cm}^3) \left(\frac{1}{5 \times 10^{+3}} \text{ cm}^{-1} \right) \quad (13)$$

$$J_{\text{max}} = 1.7 \times 10^{-9} \text{ mole/cm}^2 \cdot \text{s} \quad (14)$$

$$\text{Area} = (100) \pi (0.005)^2 \text{ cm}^2 \quad (15)$$

$$= 7.9 \times 10^{-3} \text{ cm}^2 \quad (16)$$

$$J_{\max}^{O_2} A = 1.4 \times 10^{-11} \text{ mole-}O_2/s \quad (17)$$

Thus, in this case, the diffusion limit for O_2 is sufficient to support the observed corrosion rate.

The previous calculation showed that for a large cathodic area, the corrosion rate was not limited by the diffusion of O_2 through the paint; however, diffusion can still be limiting since the H^+ and OH^- ions must diffuse through the paint film toward each other to complete the electric current path. Ignoring the term involving the concentration gradient for the moment, we can write

$$i = \kappa \frac{d\phi}{dr} \quad (18)$$

where i = current density

κ = conductivity

$\frac{d\phi}{dr}$ = gradient in potential.

For this calculation a rather generous value of $\kappa = 10^{-10} \Omega^{-1} \text{cm}^{-1}$ has been assumed. Integration of equation 18 at fixed current yields:

$$\Delta\phi = \frac{I}{2\pi\tau\kappa} \ln\left(\frac{r_2}{r_1}\right) \quad (19)$$

where I = total current

τ = paint thickness

κ = conductivity

and $\Delta\phi = \phi|_{r=r_2} - \phi|_{r=r_1}$

The potential difference has been measured around the filiform head and found to be about 0.2 mV (6). Solving equation 19 for r_2/r_1 yields:

$$\ln\left(\frac{r_2}{r_1}\right) = 1.54 \times 10^{-8} \quad (20)$$

$$\text{and } \frac{r_2}{r_1} = 1.0000000 \quad (21)$$

This result indicates that the cathodic area is confined to an area much smaller than 100 times the active head area, and this smaller area is in fact much smaller than that necessary to support corrosion on the basis of O_2 diffusion to the metal surface through the paint film.

If equation 10 is solved for $\Delta\phi$ at a value of $r_2/r_1 = 1.1$, the following result is obtained:

$$\Delta\phi = 1.23 \times 10^3 V \quad (22)$$

This is clearly an unreasonable result and represents a potential gradient of 2.5×10^6 V/cm. These simple calculations clearly indicate that the cathodic area surrounding the active filiform head is not the primary reactive surface and in fact is only a small incidental contribution to the total corrosion current.

Since there appears to be no possibility that the active cathodic area is outside the filiform head, both the primary anodic and cathodic areas must be inside the head. The possibility that oxygen is diffusing through the paint and aqueous phase into the head will now be investigated. The maximum diffusion flux through the paint with zero oxygen activity just inside the paint film has already been calculated in equation 14. The area of the head is approximately

$$A_H = \pi (0.005)^2 \text{ cm}^2 \quad (23)$$

$$= 7.85 \times 10^{-5} \text{ cm}^2 \quad (24)$$

Therefore, the maximum flux of oxygen through the paint into the head is calculated to be:

$$J_{\max} A_H = 1.34 \times 10^{-13} \text{ mole-}O_2/s \quad (25)$$

This is marginally sufficient to sustain the corrosion current; however, no account has been made of the considerable resistance to diffusion in the aqueous phase.

Another possibility exists, however. Oxygen can enter the head by diffusing up the tail. If the tail is assumed to be a half cylinder,

the diffusion area is:

$$A = \frac{1}{2}\pi (0.005)^2 \text{ cm}^2 \quad (26)$$

$$= 3.93 \times 10^{-5} \text{ cm}^2 \quad (27)$$

The density of the anhydrous reaction product FeO(OH) is:

$$\rho = 4.28 \text{ g/cm}^3 \quad (28)$$

The new volume, formed as the head progresses, is generated inside the tail at a rate expressed as:

$$r_v = vA \quad (29)$$

where r_v = rate of volume increase

v = velocity of the head

and A = area of tail cross section.

Substituting for the area and velocity yields:

$$r_v = (2 \times 10^{-7} \text{ cm/s})(3.93 \times 10^{-5} \text{ cm}^2) \quad (30)$$

$$r_v = 7.85 \times 10^{-12} \text{ cm}^3/\text{s} \quad (31)$$

From equation 3, the number of moles of iron corroding each second is:

$$N = 1.41 \times 10^{-13} \text{ mole-Fe/s} \quad (32)$$

Combining equations 32 and 28 yields:

$$V_p = 1.84 \times 10^{-12} \text{ cm}^3/\text{s} \quad (33)$$

where V_p = volume of corrosion products. From this calculation, the tail is about 77% void.

Now the diffusion rate of oxygen to the head through the tail can be calculated. The diffusion coefficient of O_2 in air is taken to be:

$$D_{\text{O}_2} = 0.178 \text{ cm}^2/\text{s} \text{ at } 0^\circ\text{C} \quad (34)$$

Correcting for temperature to 25°C yields:

$$D_{O_2} = 0.209 \text{ cm}^2/\text{s} \text{ at } 25^\circ\text{C} \quad (35)$$

The maximum rate of oxygen diffusion will occur when the gas phase oxygen concentration at the head is zero. Assuming this condition, the maximum rate of oxygen transport to the head can be calculated for the rather long filament of 15 cm as follows:

$$A J_{\max O_2} = D_{O_2} \frac{C_{O_2}}{\ell} A \quad (36)$$

where A = free area of tail cross section

C_{O_2} = O_2 concentration in air

ℓ = tail length

D_{O_2} = O_2 diffusivity in air

and $J_{\max O_2}$ = maximum O_2 flux through the tail.

Substituting for the variables yields:

$$A J_{\max O_2} = \frac{(0.209 \text{ cm}^2/\text{s})(8.6 \times 10^{-3} \text{ mole}/\ell)(10^{-3} \ell/\text{cm}^3)(0.77)(3.93 \times 10^{-5})(\text{cm}^2)}{15 \text{ cm}} \quad (37)$$

$$A J_{\max O_2} = 3.63 \times 10^{-12} \text{ mole-}O_2/\text{s} \quad (38)$$

Applying the stoichiometric factor of 4/3 (equation 9) this is equivalent to an iron flux of

$$A J_{\text{eq. Fe}} = 4.84 \times 10^{-12} \text{ mole-Fe/s} \quad (39)$$

which is 34 times the required oxygen to supply the observed corrosion rate.

The preceding discussion concerning the diffusion of oxygen can be extended to include water. The essential feature being that although the diffusion length through the tail is about 10^4 times greater than through the paint, the ratio of the gas phase diffusivity to that in the paint phase is

$$\left(\frac{D_{\text{air}}}{D_{\text{paint}}} \right)_{\text{H}_2\text{O}} \geq \frac{0.24 \text{ cm}^2/\text{s}}{10^{-6} \text{ cm}^2/\text{s}} \quad (40)$$

$$\geq 2.4 \times 10^5 \quad (41)$$

Diffusivities of water through paint as low as $10^{-9} \text{ cm}^2/\text{s}$ may be expected for the modern epoxies, polyurethanes, etc. These results clearly indicate that the primary diffusion path associated with the growth of filiform corrosion is through the tail.

The question may arise as to what force is detaching the paint from the metal. Could this force be hydrostatic in nature produced by the osmotic pressure generated when water diffuses into the head through the paint? An estimate can be made of the maximum pressure in the filiform head by considering the pressure drop which can be supported in the tail. First the rate of water diffusion into the head will be considered.

The maximum rate of water diffusion into the head can be estimated for the case of 95% relative humidity air and a 2.0 molal FeCl_2 solution inside the head. Robinson and Stokes (7) give the osmotic coefficient for the FeCl_2 solution as

$$\phi = 1.371 \quad (42)$$

This leads to an activity of water as follows:

$$\ln a_w = \frac{-(3)(2)(18.016)1.371}{1000} \quad (43)$$

$$= 0.148 \quad (44)$$

$$a_w = 0.862 \quad (45)$$

The concentration of water vapor at 95% RH and 25°C is as follows (8):

$$C_{H_2O} = 21.9 \text{ g/m}^3 \quad (46)$$

At 86.2% RH we calculate:

$$C_{H_2O} = 19.9 \text{ g/m}^3 \quad (47)$$

The area for water diffusion is approximately 25% of the area of a sphere of radius $5 \times 10^{-3} \text{ cm}$. Thus

$$A = 7.85 \times 10^{-5} \text{ cm}^2 \quad (48)$$

For water diffusing through the paint into the head the water flux is thus calculated to be

$$N_{H_2O} = \frac{(10^{-6} \text{ cm}^2/\text{s})(2.0 \text{ g/m}^3)(10^{-6} \text{ m}^3/\text{cm}^3)(7.85 \times 10^{-5} \text{ cm}^2)}{5 \times 10^{-3} \text{ cm}} \quad (49)$$

$$N_{H_2O} = 3.14 \times 10^{-14} \text{ g-H}_2\text{O/s} \quad (50)$$

Now, if we presume the tail to be a cylinder of cross sectional area,

$$A = (0.77)(3.93 \times 10^{-5} \text{ cm}^2) \quad (51)$$

$$= 3.03 \times 10^{-5} \text{ cm}^2 \quad (52)$$

the equivalent radius is calculated to be

$$r_e = 3.10 \times 10^{-3} \text{ cm} \quad (53)$$

Pure water will be assumed, with a viscosity of

$$\mu_{H_2O} = 0.89 \text{ cP} \quad (54)$$

The Hagen-Poiseuille equation can now be solved for the pressure drop through the tail.

$$\frac{\Delta P}{L} = \frac{8 \mu Q}{\pi r_e^4} \quad (55)$$

where μ = viscosity of water

Q = volumetric flow rate

$\frac{\Delta P}{L}$ = pressure drop/length

and r_e = radius of the tube.

$$\frac{\Delta P}{L} = \frac{(8)(0.89 \times 10^{-2} \text{ g/cm}\cdot\text{s}) (3.14 \times 10^{-14} \text{ cm}^3/\text{s})}{\pi (3.10 \times 10^{-3})^4 \text{ cm}^4} \quad (56)$$

$$= 7.67 \times 10^{-6} \text{ g/cm}^2 \text{s}^2 [=] \text{ Dyne/cm}^2 \cdot \text{cm} \quad (57)$$

$$\frac{\Delta P}{L} = 7.57 \times 10^{-12} \text{ Atm/cm} \quad (58)$$

Thus even for a relatively long (10 cm) filament, the pressure drop is very small ($\approx 10^{-10}$ Atm). Clearly, some other mechanism is responsible for lifting the paint from the metal surface. This may be anodic undermining of the paint or possibly a mechanical force generated by the precipitation of the reaction products at the back of the head.

References to the Appendix

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