

AN ABSTRACT OF THE THESIS OF

STEVEN EDWARD HOOVER for the MASTER OF SCIENCE
(Name of student) (Degree)

in Chemistry (Physical) presented on June 3, 1971
(Major)

Title: A MECHANISM FOR FILIFORM CORROSION OF ALUMINUM
Redacted for privacy

Abstract approved _____
Dr. W. H. Slabaugh _____

A mechanism for filiform corrosion of aluminum is proposed based on experimental evidence and the known aqueous chemistry of the trivalent aluminum ion. Experimental methods utilized include autoradiographs with Cl^{36} ; pH paper determination of the filiform head pH; activator concentration and activation period as they affect filiform growth.

The pH of the active filiform head was determined to be 1.5 - 2.0 pH units. An activator concentration of 0.1 N HCl was the minimum amount necessary to initiate good filiform growth and an activation period of at least 180 seconds was also necessary to initiate good filiform growth. Autoradiographs showed a small amount of Cl^{36} remaining in the corrosion product with the heaviest concentration present in the filiform head.

Activation occurs at a break or weak point in the film. Due to osmotic pressure, water enters this area causing film separation and

an electro-chemical corrosion cell is formed. Aluminum is dissolved at the anode, going into solution as the trivalent aluminum ion. This ion hexa-hydrates, accounting for the low pH value in the head due to its acidic nature. Simultaneous products of hydrogen gas and hydroxide ion are formed at the cathode utilizing water and oxygen in the process. Due to mixing and convection within the cell, the Al^{+++} precipitates as $\text{Al}(\text{OH})_3$ at the transition boundary when the solubility product is exceeded and the corrosion product is deposited with a subsequent loss of water to the atmosphere.

Insufficient relative humidity causes the boundary to catch the head and the cell dies while an excess of relative humidity will result in blisters and general corrosion. Excess oxygen will also increase the rate and extent of filiform growth.

A Mechanism for Filiform Corrosion of Aluminum

by

Steven Edward Hoover

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1972

APPROVED:

Redacted for privacy

Professor of Chemistry

Redacted for privacy

Chairman of Department of Chemistry

Redacted for privacy

Dean of Graduate School

Date thesis is presented June 3, 1971

Typed by Ilene Anderton for Steven Edward Hoover

ACKNOWLEDGEMENTS

The author would like to express his appreciation to Dr. W. H. Slabaugh for his recommendations, inspiration and patience during the course of this investigation.

The author would also like to extend a special amount of appreciation to his wife, Ginny, whose help and support made the last two years enjoyable.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
LABORATORY STUDY OF FILIFORM	6
Experimental Methods	6
Preparation of Panels	6
Methods of Studying Filiform Corrosion	7
EXPERIMENTAL RESULTS	12
Filiform Head pH Measurements	12
Filiform Growth as a Function of Activator Concentration	13
Filiform Growth as a Function of Activation Period	14
Filiform Activator Traced with Radioactive Cl ³⁶ Through Autoradiographs	16
DISCUSSION OF EXPERIMENTAL RESULTS	20
SUMMARY	28
BIBLIOGRAPHY	29

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Panels positioned in the modified vacuum desiccator.	10
2	Filiform growth as a function of activation period.	15
3	Results of Cl^{36} autoradiographs.	18
4	An active split filiform head with hydrogen gas bubbles.	23
5	Effect of excess oxygen on filiform growth.	24
6	Diagram of a growing filiform filament	25

A MECHANISM FOR FILIFORM CORROSION OF ALUMINUM

INTRODUCTION

Filiform corrosion, sometimes termed "underfilm" corrosion, is a filament type of corrosion of metal materials. It occurs on metals when coated with organic coatings and exposed at a relative humidity range of 60-95%. This type of corrosion was descriptively named by Sharman (10) and adequately described by Van Loo and coworkers (15). Filiform corrosion differs from ordinary corrosion in several characteristics. Filiform corrosion grows in definitely defined filaments; the growing filament has a defined "head" where the active corrosion occurs; the head is distinguished from the "body" by the liquid appearance of the head as opposed to the dry stable corrosion product in the body; and these filaments seldom cross each other. When a growing filament strikes an old filiform track, it either bends and grows in a different direction or it "dies". It was observed by Van Loo (15) and his collaborators that when the active head of one filiform meets the inactive body of another, it is deflected in its growth path. When two filiform heads meet, they may blend and continue growing as a single filament.

Van Loo, Laiderman and Bruhn (15) have observed filiform corrosion not only on iron and steel, but also on magnesium and

aluminum. Filiform will grow under organic films only when they are formulated below their critical pigment volume concentrations (1) where the film serves as a semipermeable membrane. It has also been reported that filiform growth can occur on surfaces not covered with an organic coating, such as under tinplate, silverplate, goldplate and certain phosphate coatings on steel. Filiform will also grow under oxide coatings of certain metals.

Van Loo (15) and collaborators proposed a mechanism for filiform corrosion in which an anodic area is formed which lifts the film off the surface of the metal. Air and moisture pass into this area and a solution of the hydrated metal ion is formed, which upon desiccation, forms the stable corrosion product. This growth of filiform continues as a result of the development of an oxygen concentration gradient between the head, which contains less active oxygen, and the filament body.

According to Van Loo (15), the width of the tracks increase with the thickness of the organic coating and with increased humidity. Sharman (10) stated that the shape of the bubble, or head of the filament, was determined by the adhesion between the coating and the surface. Later work by Lobanov, Shterenzon and P'yankova (8), found the steady state metal corrosion rate independent of the adhesion of the film to the metal. Instead, the rate of growth was fixed by the permeability of the polymer film to water and hydrochloric

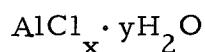
acid, which they employed as a corrosive media. Slabaugh and Kennedy (13) have confirmed these results with regard to the semi-permeable properties of films necessary for good filiform growth.

A study of filiform corrosion induced by different salt nuclei, for example sodium chloride, ammonium sulfate, ammonium chloride, and calcium sulfate, at various humidities was conducted by Preston and Sanyal (9). Initiation of corrosion by nuclei, according to the authors, follows the adsorption of water vapor on the surfaces of the salt nuclei forming a saturated solution which corrodes by the electrolytic process. Similar work has also been conducted by Kaesche (6) in Germany. His investigation, again by the induction of salt nuclei, showed the average diameter of individual filaments increased with atmospheric moisture. Kaesche also observed that very wide filaments proceed over smaller ones.

Earlier work by Slabaugh and Grotheer (12) on filiform corrosion established anodic and cathodic areas on the metal surface. The electro-potentials between the anodic and cathodic areas were measured. In this study on steel panels, it was found the head is always anodic to the rest of the surface of the exposed metal. According to Slabaugh and Grotheer, formation of the corrosion cell, or growing head, results in the disengaging of the film from the metal due to osmotic action. The driving force of this type of corrosion is controlled by the osmotic action in the growing cell.

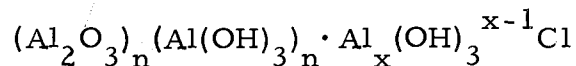
In a study by Godard and Torrible (4), the aggressiveness of chloride ions on the oxide film of aluminum was studied with respect to the effect of sulfate ions on similar films. They concluded that the chloride ion was much more active toward the aluminum oxide layer and in a proposed mechanism, should result in an increased hydroxide ion concentration in solution. Heine and Keir (5) suggested that the substitution of chloride ions for oxygen ions at specific locations in the aluminum oxide film, caused an increase in the rate of metal oxidation and film dissolution at these sites. At higher chloride ion concentrations, the film broke down at an increased rate with the subsequent formation of deeper corrosion pits in the metal surface. According to Aziz (2), chloride ions also have a specific peptizing action on alumina, thus preventing effective protective film formation.

As corrosion takes place on the surface of the metal, in more concentrated solutions, a loose white powder forms as the corrosion product. Lobanov, Shterenzon, and P'yankova (8) concluded that this product was a hydrated aluminum chloride of the formula,

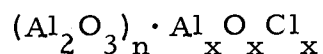


and reflected the use of only water and hydrochloric acid in the corrosion process. The ratio of x and y in this formula is an apparent ratio in the more dilute acids, for a fraction of the corrosion product may be due to the use of oxygen in the corrosion. Lepin and Kadek (7) postulated that the primary oxide film is first changed at the

surface to the oxychloride variety, the structure of which might be represented by the formula,



or, in the absence of the hydrated forms of the oxide,



Where this primary oxide film breaks down, deposits of bayerite ($\alpha\text{-Al}(\text{OH})_3$) and boehmite ($\gamma\text{-AlO}(\text{OH})$) develop. They attribute this to a mixed oxidation mechanism of aluminum due to water and oxygen and is independent of the chloride concentration.

Many of the references thus far mentioned were based on filiform corrosion studies on ferrous metal materials. Due to the lack of work on filiform corrosion of aluminum, these sources were used as background and all acknowledged material also applies to the present work.

At present, there is no adequate solution to the problem of inhibiting filiform corrosion. With an adequate theory as a guide, it is anticipated that a successful method of controlling filiform corrosion of aluminum can be found. Thus, the present work is primarily concerned with supplying a workable theory for the mechanism of filiform corrosion of aluminum.

LABORATORY STUDY OF FILIFORM

Experimental Methods

Preparation of Panels

Panels used in this study were 3" x 3" panels of 2024 alclad aluminum. Before coating, the panels were individually hand wiped with acetone in order to remove grease and marking dye. Next, they were dipped in a mixture of 100 ml 70% nitric acid, 20 ml 48% hydrofluoric acid, and 1000 ml distilled water until a break-free surface film of water was obtained. A double rinse in distilled water followed. After air drying, the panels were coated with XYSG from Union Carbide, or polyvinyl butyral. The composition of the coating mixture was as follows; 125 ml n-butyl alcohol, 500 ml 95% ethanol, and 50 gm XYSG powder. Coating was accomplished by hand-dipping until a coat of minimum dry thickness of 0.08 mm per side was obtained. After drying overnight, the panels were ready for activation. A small drop of concentrated hydrochloric acid was applied with an eyedropper to an eighth inch hole drilled through the panel in order to activate filiform growth. The size of the drop was determined by the amount of liquid which would remain in the hole due to surface tension.

Panels thus activated were placed in glass desiccators, which

were chosen as containers for the following several reasons; with proper lubrication, this closed container provides a sealed system for a reasonably long period of time; and it permits observation during the course of filiform growth. A saturated solution of monobasic ammonium phosphate was placed in the bottom of the desiccators. This saturated monobasic ammonium phosphate solution provided a constant relative humidity of 92% at a temperature of 20° C.

Methods of Studying Filiform Corrosion

In order to ascertain the pH of the active filiform head, several methods were used. The first utilized narrow range pH paper. Working with a microscope and a small piece of pH paper moistened with distilled water, a cut was made with a scalpel at the side of the head and the pH paper was inserted. Immediate color comparison of the pH paper with supplied reference charts gave the desired pH value present in the filiform head. The second method involved coatings impregnated with indicators. An indicator of the appropriate range was dissolved in the coating material, then panels were dipped in this mixture until a satisfactory coating was obtained. One variation of this method was employed where the indicator was dissolved in acetone, and then applied to the bare panels while in a horizontal position. After solvent evaporation, a thin coating of indicator remained on the panels. Panels were then dipped in the regular XYSG coating

material. Normal initiation and growth procedures followed in all cases.

Effects of initiator concentration and duration of initiation were studied through appropriate tests. Varying concentrations of hydrochloric acid ranging from 0.01 N to 12 N or concentrated, were used to initiate a group of panels in the normal manner. A similar test was made using concentrated hydrochloric acid and varying duration times of initiation. After the application of a drop of acid to the panel, excess liquid was removed by means of a Kimwipe after the following time periods; immediately following application, 60 seconds, 180 seconds, and not removed. Normal growth conditions followed in all cases and filiform growth was observed and rated by the amount of growth present on the panels.

Radioactive Cl^{36} in the form of hydrochloric acid was employed as a tracer to follow the activating agent during filiform growth. A strong beta emitter with a half-life of 3×10^5 years, Cl^{36} was ideally suited to this experiment. Eight panels coated with XYSG were activated using a hypodermic syringe with a drop of 0.27 N hydrochloric acid manufactured by New England Nuclear with radiometric purity of 99%.

Panels thus activated were placed in a plexiglass holder where they were held in a vertical position approximately 1.5 cm apart. This holder, with panels, was then placed in a modified vacuum

desiccator (see Figure 1) in which humidity control was provided by a saturated solution of monobasic ammonium phosphate placed in the bottom. A small amount of solid carbon dioxide, approximately 1-1.5 gm, was also placed in the desiccator in order to maintain a mixed atmosphere. Previous work done in our laboratory showed the amount of carbon dioxide present was not critical as long as oxygen was present in the atmosphere of the container. The top was well sealed with Apieson M grease. Pure oxygen was flushed through the system for a period of two minutes through tube A, with tube B open to the room (see Figure 1). Tube B was sealed immediately after flushing with oxygen and tube A was sealed when the solid carbon dioxide had totally sublimed and the desiccator was at atmospheric pressure. The desiccator was removed for observation of filiform growth at room temperature.

Autoradiographs were made of the panels to determine where the radioactive Cl^{36} had been distributed during filiform growth. Following a 35 day growth period, the panels were removed from the desiccator. The autoradiographs were exposed in large film cassettes in the following manner; a sheet of Kodak X-ray film was placed in the bottom of the cassette; an equivalent sized piece of Saran Wrap, whose purpose was to keep contamination and corrosion products from the panels off the film and cassette, followed; the panels were placed on top of the Saran Wrap; a second piece of Saran

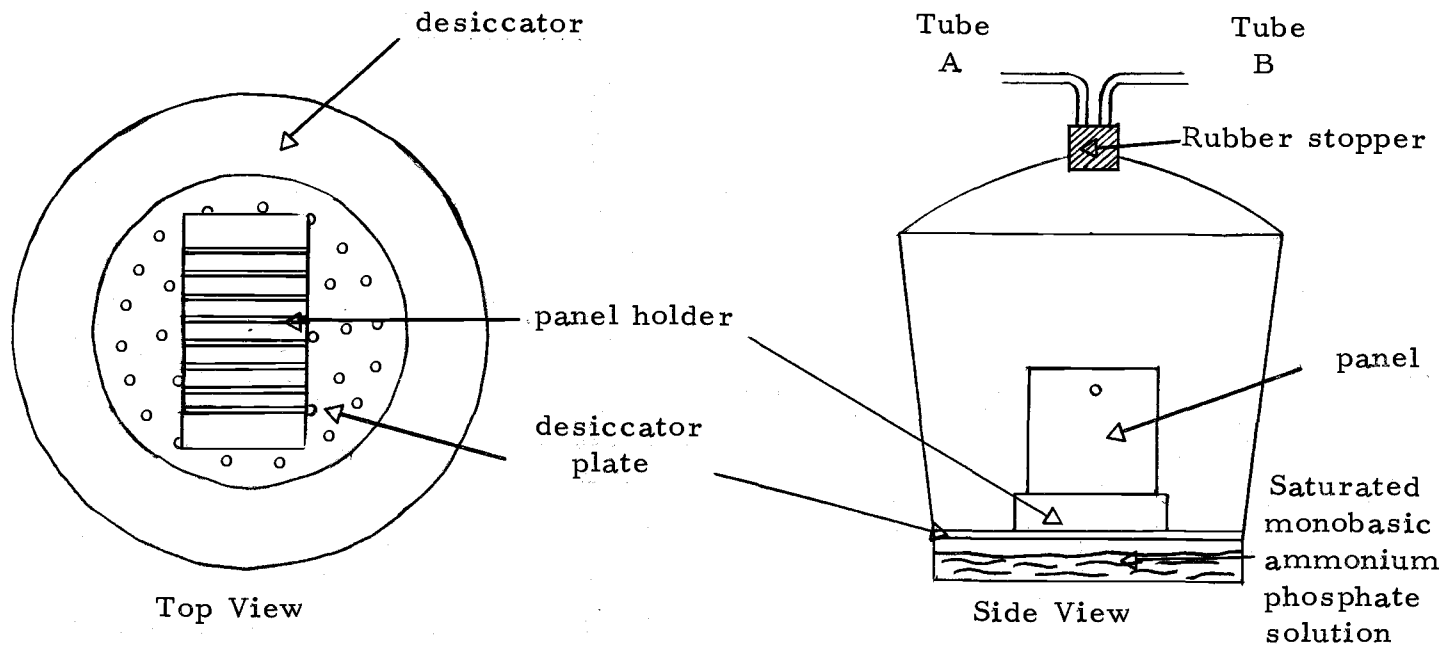


Figure 1. Panels positioned in the modified vacuum desiccator.

Wrap was placed on top of the panels; the top sheet of Kodak X-ray film was placed on top of the panels and the cassette was closed.

They were set aside for exposure at room temperature.

Two sets of autoradiographs were exposed, one set with an exposure period of five days and the second set with an exposure period of 34 days. Following exposure, the X-ray films were developed and allowed to dry. Color 35 mm slides were made of both sides of each panel used in this study. These were then compared with the autoradiographs by projecting the slide pictures on the back of the X-ray films. Concentrations of Cl^{36} , visible on the autoradiographs, could be directly related to corrosion patterns on the panels.

EXPERIMENTAL RESULTS

Filiform Head pH Measurements

Narrow range pH paper covering the entire pH range of 0-14 pH units was used to ascertain the pH of the active filiform head. Due to the unpredictable nature of filiform corrosion growth, it was difficult to find panels with growing filiform heads satisfactory for this study. Many filaments had an insufficient amount of liquid in the head for a measurement and many more had died before they were studied. Following numerous attempts to grow filiform corrosion with the proper active liquid heads, one group of panels with active heads satisfactory for this study were finally grown and used for this study. These heads were known to be active due to the visible evolution of hydrogen bubbles from the leading edge of the head. Measurements made on these heads in the manner previously outlined indicated an active filiform head pH of 1.5-2.0 pH units. This pH value is actually reduced somewhat in the cell, because in order to measure cell pH, it was diluted due to the moistened pH paper. A true value of 0.5-1.0 pH units probably represents the cell pH.

The following indicators, with pH ranges, were used in both sections of the impregnated indicator study; Methyl Violet 0.0-1.6; Methyl Green 0.2-1.8; Metacresol Purple 1.2-2.8; Congo Red

3.0-5.0; Methyl Orange 3.2-4.4; and Bromocresol Green 3.8-5.4. In the first section, panels coated with mixtures of these indicators and XYSG were activated in the normal manner. The coating of indicator deposited by acetone in the second section was very thin because too much would crack and peel off when the solvent evaporated. Once the coating of indicator was on the panel's surface, XYSG was applied by two methods. The first involved application with a spray gun and the second method was hand dipping. In both cases, the deposited indicator redissolved and dispersed in the XYSG coating material. After drying, these panels were activated in the normal manner. All panels used in this study had good filiform corrosion growth, but no color change occurred in any indicator used where a filament grew. Apparently, the indicator was not soluble to a sufficient extent to be affected by the pH in the filament head, or in the second section, an insufficient amount of indicator remained at the metal-coating interface to be affected by the pH of the filament head.

Filiform Growth as a Function of Activator Concentration

Panels activated with varying concentrations of hydrochloric acid had a uniform amount of filiform growth down to, and including, panels with an activator concentration of 0.1 N. Below a concentration of 0.1 N, the panels had only a very small amount of filiform growth. This result is supported by the work of Lepin and Kadek (7)

with KCl solutions which indicate that 0. 1N is a transition point for adequate corrosion growth at room temperature.

Filiform Growth as a Function of Activation Period

Three sets of panels were activated for varying time periods in order to ascertain any relationship between the period of activation and the subsequent amount of filiform corrosion growth. Identical results were obtained with all three sets of panels. Panels on which the activator was removed immediately after application had a very small amount of filiform corrosion, likewise for the panels with an activation period of 60 seconds. A three minute activation period gave a small amount of filiform corrosion and panels where the activator was not removed, all had normal amounts of filiform corrosion growth (see Figure 2). It would appear that time is a significant factor involved in the activation of panels for filiform corrosion using this method. The longer the activation period, a greater amount of aluminum and oxide coating would be dissolved in the area surrounding the activation point. Thus, the corrosion cell would be well started by a higher concentration of ions in solution, which would be the case with a longer activation period resulting in a greater amount of filiform corrosion growth.

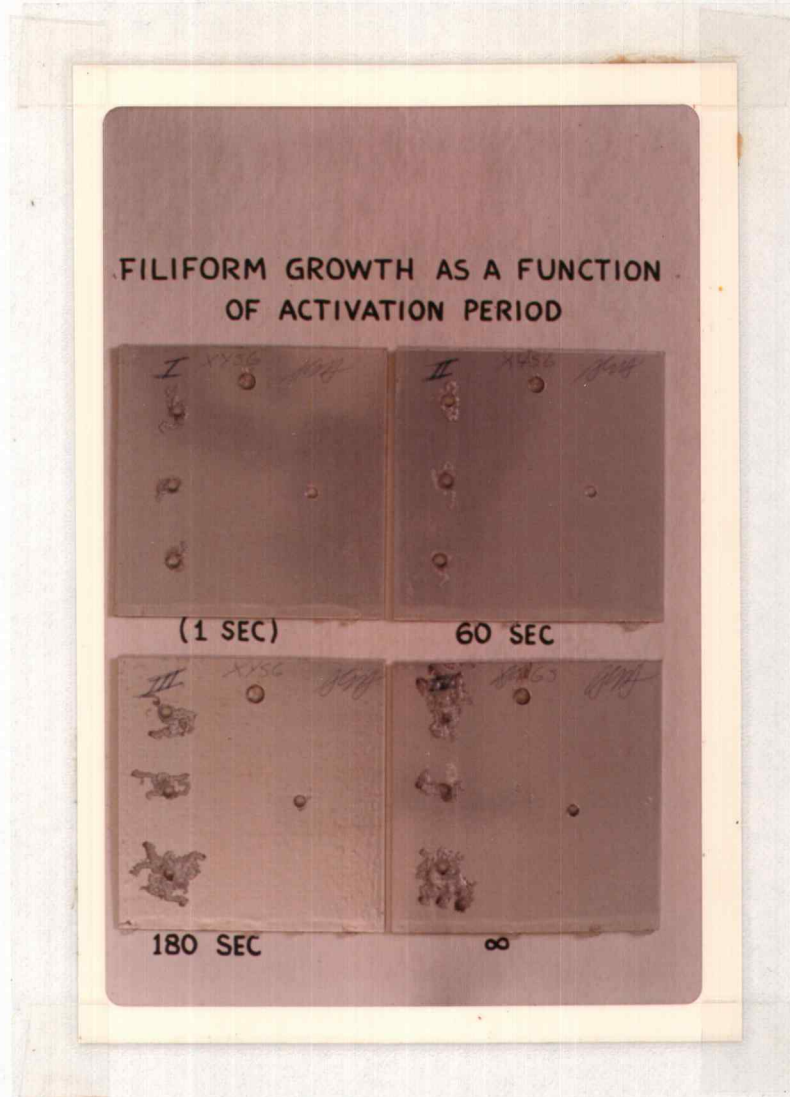


Figure 2. Filiform growth as a function of activation period.

Filiform Activator Traced with Radioactive Cl³⁶
Through Autoradiographs

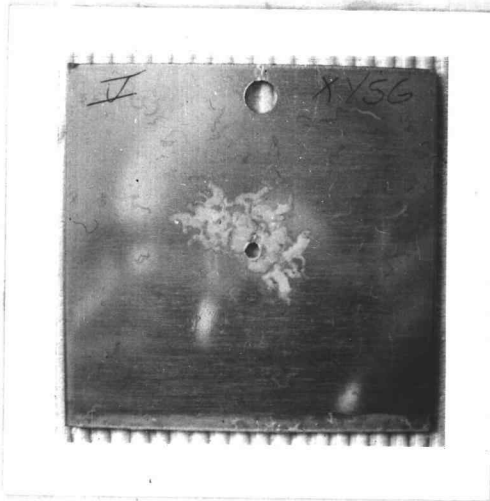
Autoradiographs were used to trace the activator, in the form of radioactive hydrochloric acid, to determine where it went during filiform growth. Two problems occurred during this study, the first of which involved the activation of the panels. Following activation in the normal manner, sometimes the drop of acid would run out of the hole and down the surface of the panel where evaporation would take place. When the autoradiographs were made, this appeared as a spot where the Cl³⁶ was concentrated, but there was no corrosion on the panel corresponding to it. Thus, any exposed spots in a vertical line below the activation point which do not correlate to the corrosion on the panels were due to this type of spilling.

The second problem occurred during the exposure of the X-ray film. This type of film responds to radiation, but if physical pressure is applied, it will also give the appearance of normal exposure when developed. Due to the limited space within the cassettes when closed, the corrosion products which were raised above the panel's surface caused pressure points against the film. Thus, when the autoradiographs were developed, there were several areas of exposure due to pressure which blocked the actual results. Fortunately, this type of exposure was kept at a minimum and sufficient information

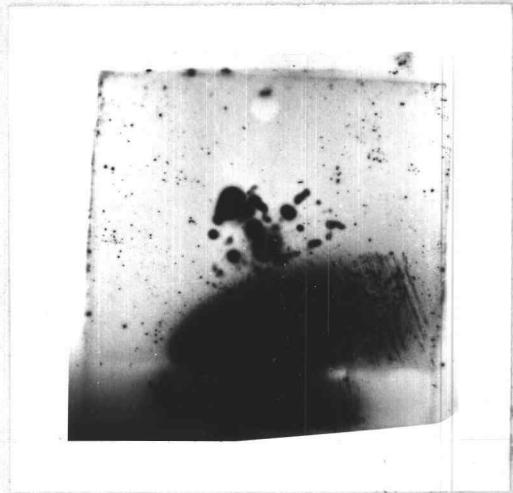
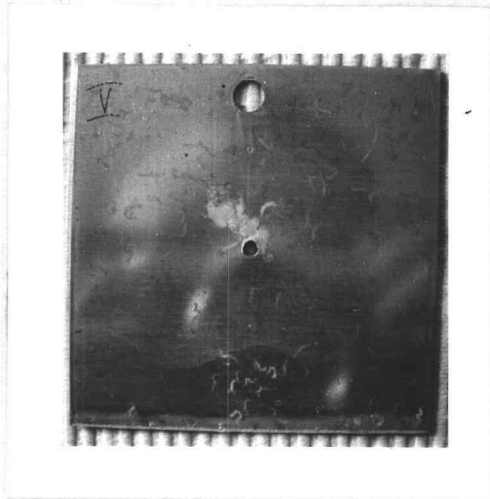
was obtained to ascertain the fate of the activator.

When the first set of autoradiographs with an exposure time of five days was compared with the actual corrosion of the panels, there was excellent agreement between the corrosion pattern on the panels and the autoradiographs. In most cases, the concentrations of Cl^{36} corresponded to the filament heads. Several autoradiographs contained extraneous spots of exposure, but these were ascertained to be of the type caused by activation spilling. It was also noted that the corrosion patterns from the front of the panels also faintly exposed the backside autoradiographs and visa versa. All of the autoradiographs in this set indicated that the activator was carried along only in the liquid corrosion cell with very little remaining at the activation point (see Figure 3).

The second set of autoradiographs with an exposure time of 34 days gave similar results to the first set with one exception. Due to a longer exposure time, smaller concentrations of Cl^{36} appeared on the autoradiographs when developed. This set indicated that a small amount of Cl^{36} remained in the corrosion product as the filament grew. This is supported by Lepin and Kadek (7) who concluded that the aluminum oxychloride was formed in small amounts during the corrosion process. Thus, it would appear that although the activator is carried along in the liquid corrosion cell, a small portion of it remains in the corrosion product, thereby decreasing the



FRONT



BACK

Figure 3. Results of Cl^{36} autoradiographs.

concentration of Cl^{36} in the cell as the filament grows.

An interesting discovery concerning the extent of activator migration was made during the course of this investigation. All panels activated in the normal manner showed small traces of Cl^{36} over the entire surface on both sides. This could have only been due to the evaporation of the hydrochloric acid activator and subsequent re-depositing on the panels due to the high humidity present in the growth chamber. If filiform growth occurred over the entire surface of the panels, this would correspond to vapor activation which was an earlier method used to activate filiform corrosion growth.

DISCUSSION OF EXPERIMENTAL RESULTS

Based on the results of this investigation and the work of others, a mechanism for filiform corrosion of aluminum can be formulated. The first step to consider is the activation of filiform corrosion. This occurs where a weak point, or break, is present in the coating on the aluminum surface and sufficient quantities of water and activator have accumulated. At this point, a typical electro-chemical corrosion cell is formed and the corrosion process is started. By using concentrated hydrochloric acid as an activator, the rate of corrosion growth is accelerated by the rapid formation of a large amount of electrolytic solution due to the dissolution of the aluminum and oxide coating by the acid. Hence, an excellent start has been made toward good filiform formation.

Since filiform corrosion occurs only above 65% relative humidity on steel, according to Slabaugh and Grotheer (12), it is suggested that the concentration in terms of mole fraction of solute of the cell fluid must be high enough to cause a diffusion of moisture from the atmosphere, through the film, and into the corrosion cell. The water in the cell has diffused through the film by osmosis, and therefore the water vapor pressure on the atmosphere side, P_1 , must slightly exceed the vapor pressure on the liquid side, P_2 .

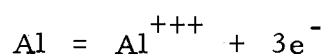
$$P_1 > P_2$$

If P_2 will be only slightly smaller than P_1 , the approximate mole fraction concentration of the cell fluid can be calculated from Raoult's law.

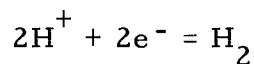
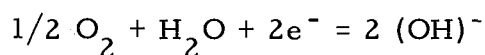
$$\frac{P - P_2}{P} = \frac{n_2}{n_1 + n_2} = N_2$$

where N_2 is the minimum mole fraction of solute in the cell fluid, P is the vapor pressure of pure solvent (water) and n_2 is the number of moles of solvent.

The electrochemical processes that occur within the growing filiform filament are those associated with the corrosion reaction of aluminum in the presence of water and oxygen. At the anode, the reaction which occurs is that of aluminum going into solution as tri-valent aluminum ions.



The cathodic part of the corrosion cell yields two reactions, both occurring simultaneously:



Experimental evidence supporting these reactions was obtained through the use of time-lapse films of active filiform growth produced by others in this laboratory. Physical changes such as the dissolution of metallic aluminum and the evolution of hydrogen bubbles were

readily apparent (see Figure 4). The concentration of oxygen was shown to affect filiform growth. Activated panels placed in oxygen-free growing atmospheres exhibited no filiform growth, while panels placed in atmospheres containing excessive amounts of oxygen showed rapid and extensive filiform growth (see Figure 5).

It is now possible to outline the driving mechanism for filiform corrosion of aluminum. Once activated, osmotic action of water will cause the film to disengage from the metal surface due to the pressure difference and the corrosion cell is formed. An additional factor causing film disengagement is the pressure created by hydrogen gas evolution within the cell. The distinctive shape of filiform corrosion is probably due to a combination of osmotic pressure and the adhesive strength of the film, both of which cause the filiform head to move in a narrow path in a random direction.

At point A of a growing filament (see Figure 6), the concentration of aluminum ions is very high and hence the osmotic rate is also quite high because P_1 is much greater than P_2 . As the cell grows, the fluid becomes diluted due to additional moisture entering the cell by osmosis. When the aluminum hydroxide is precipitated at the transition boundary, point B, the concentration is rapidly diminished and the vapor pressure is reversed with P_2 greater than P_1 . Thus, moisture is removed from the cell at point C to the atmosphere and the relatively dry, stable corrosion product remains.



Figure 4. An active split filiform head with hydrogen gas bubbles.

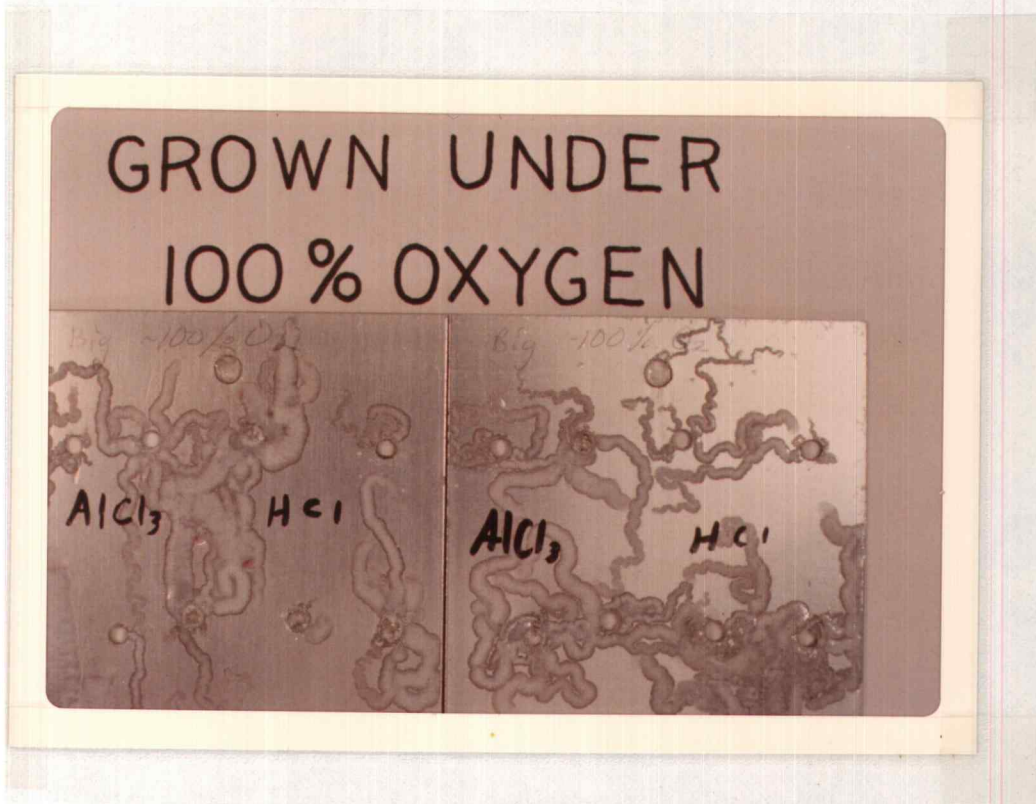


Figure 5. Effect of excess oxygen on filiform growth.

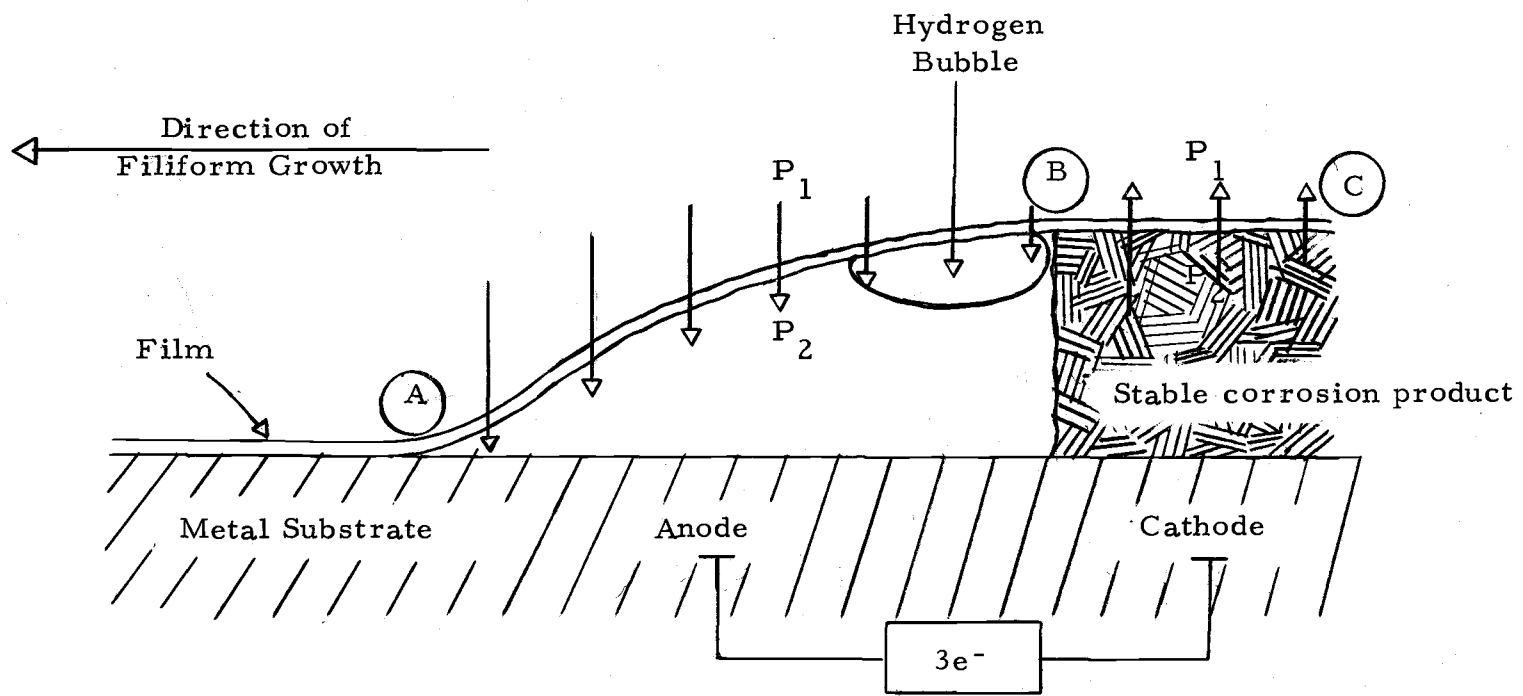
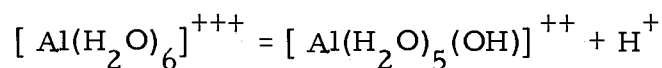


Figure 6. Diagram of a growing filiform filament.

This type of action causes the cell to move forward at a relatively constant width due to the transition boundary, point B, being able to keep up with the growing head. If subjected to excessively high relative humidity, the head grows faster than the boundary can keep up and radial heads, or general corrosion is the result. If insufficient relative humidity is present, this boundary catches the head at point A and the head dies, having been converted to the corrosion product.

The pH of the growing filiform head would be expected to have a high pH based on the cathodic reactions. Since this is not the case, something else apparently contributes to lowering the pH value. It is well known that aqueous solutions of trivalent aluminum ions are subject to extensive hydrolysis (3). This hexa-hydrated aluminum ion is quite acidic according to the following reaction



with a disassociation constant of

$$K_a = 1.12 \times 10^{-5}$$

This accounts for the low pH value measured in the cell and prevents the $Al(OH)_3$ from precipitating at this point. When the alkaline cathodic products of reaction and the acid anodic products of reaction intermingle through a process of diffusion and convection, the pH of the cell fluid rises. At point B, the solubility product of the alumina in solution is exceeded resulting in precipitation of alumina at this

point. Water vapor will then diffuse back into the atmosphere as previously outlined.

Given constant growing conditions, filiform growth should continue until interrupted by a change in conditions. However, observation shows that filiform corrosion dies after an initial growing period. Since the temperature and humidity remained constant, cessation of growth must be due to the nature of the filiform filament. Having shown that small amounts of the activator remain in the corrosion product, perhaps the concentration is reduced below a critical point necessary for filiform growth and the filament dies. Other factors which could cause the filament to die are the pH of the head reaching a critical point or an over-concentration of alumina which totally precipitates and growth ceases. Further research will be necessary to ascertain what causes filiform growth to die naturally. Once this is done, perhaps it could be utilized as a means of inhibiting filiform growth.

SUMMARY

The mechanism proposed in this study accounts for the activation, growth, and death of filiform corrosion. Activation is caused by an electrolytic solution at a break in the film, followed by cell formation due to osmotic action. Dissolution of aluminum at the anode and formation of hydroxide ions and hydrogen gas at the cathode provide the components for the stable corrosion product, $\text{Al}(\text{OH})_3$. Relative humidity is a critical factor, keeping the boundary moving at the same growth rate as the leading edge of the cell. When these conditions depart from the critical values, filiform corrosion dies.

By examining this mechanism, several points are opened for attack in order to develop preventative measures against filiform corrosion. One approach would be the use of a non-permeable film, thus halting osmosis. Another possible measure would be the addition of a hydroxide inhibitor in the coating, thus keeping the corrosion product from forming and halting boundary movement. Both of these measures would prevent filiform corrosion from growing. Many other measures should be investigated, which when coupled with this mechanism, would hopefully provide an adequate method of prevention.

BIBLIOGRAPHY

1. Asbeck, W. K. and M. Van Loo. Critical pigment volume relationship. *Industrial and Engineering Chemistry* 41:1470-75. 1949.
2. Aziz, P. M. Views on the mechanism of pitting corrosion of aluminum. *Corrosion* 9:85-90. 1953.
3. Cotton, F. A. and G. Wilkinson. *Advanced Inorganic Chemistry A Comprehensive Text*. 2d ed. New York, Interscience Publishers, 1966. 1136p.
4. Godard, H. P. and E. G. Torrible. The effect of chloride and sulphate ions on oxide film growth on Al immersed in aqueous solutions at 25°C. *Corrosion Science* 10:135-42. 1970.
5. Heine, M. A., D. S. Keir and M. J. Pryor. The specific effects of chloride and sulfate ions on oxide covered aluminum. *Journal of the Electrochemical Society* 112:24-32. 1965.
6. Kaesche, H. Filiform corrosion of painted steel surfaces. *Werkstoffe u. Korrosion* 11:668-81. 1959.
7. Lepin, L. and V. Kadek. Conditions for disruption of the primary film during corrosion of aluminum in neutral solutions. *Corrosion Science* 6:177-81. 1966.
8. Lobanov, Yu. E., A. L. Shterenzon and L. V. P'yankova. Corrosion of aluminum protected by polymer films in hydrochloric acid. *Protection of Metals* 5:25-31. 1969. (Translated from *Zashchita Metallov*)
9. Preston, R. St. J. and B. Sanyal. Atmospheric corrosion by nuclei. *Journal of Applied Chemistry* 6:26-44. January 1956.
10. Sharman, C. F. Filiform underfilm corrosion of lacquered steel surfaces. *Nature* 153:621-22. 1944.

11. Slabaugh, W. H. and E. J. Chan. Atmospheric components and filiform corrosion. *Journal of Paint Technology* 38:417-21. 1966.
12. Slabaugh, W. H. and M. Grotheer. Mechanism of filiform corrosion. *Industrial and Engineering Chemistry* 46:1014-16. 1954.
13. Slabaugh, W. H. and G. Kennedy. Adsorption characteristics of organic films and filiform corrosion. *Official Digest of the Federation of Societies of Paint Technology* 34:1139-52. 1962.
14. Uhlig, H. H. (ed.). *The Corrosion Handbook*. New York, John Wiley and Sons, 1948. 1118p.
15. Van Loo, M., D. D. Laiderman and R. R. Bruhn. Filiform corrosion. *Corrosion* 9:277-83. 1953.