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THE CHEMISTRY OF FAILURE OF ALUMINUM ELECTROLYTIC CAPACITORS

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THE CHEMISTRY OF FAILURE OF ALUMINUM ELECTROLYTIC CAPACITORS

I. INTRODUCTION

The circuit designer may treat aluminum electrolytic capacitors as passive components, but a chemist would consider them to be potentially among the most active of devices. Some of the most common failure modes of these capacitors are the result of slow chemical and electrochemical reactions on the electrode surfaces. These reactions are an inherent property of the system and are not due to the intrusion of an aggressive contaminant. To the authors' knowledge no study of these reactions has ever been presented. The purpose of this paper is to show the relationship between particular failure modes and these electrode reactions, and to provide a detailed description of these reactions. Systems in which these reactions are essentially absent are only briefly discussed.

A. Description of System

The most common type of aluminum electrolytic capacitor consists of two aluminum foils separated by porous paper spacers; the whole wound into a cylinder and impregnated with a liquid electrolyte. This assembly is sealed into a can with the foils connected to terminal leads. The foils have been etched to increase surface area and hence capacitance. The foil connected to the positive terminal has been anodized to develop an aluminum oxide layer of sufficient thickness to withstand the required voltage stress. This oxide is the capacitor dielectric. The electrolyte provides an electrical connection between anode and cathode foils and also serves as a source of oxygen for reforming oxide dielectric that may be damaged during use of the device. References to more detailed discussions of the construction of these capacitors are found in the recent literature. 1

A requirement common to all customer specifications for these capacitors is that after a prescribed time at rated temperature both with and without applied voltage, the capacitance, dissipation factor and leakage current shall not have exceeded stipulated limits. A typical requirement is in the military specification MIL-C-62B which states that after 100 hours at 85 C with no applied voltage, the capacitance shall not have changed more than ±10% from its initial value, the dissipation factor shall not be more than 120% of the initial requirement, and the leakage current shall not exceed 200% of the initial requirement.

B. Results of Failure Analysis

In the course of developing improved low voltage capacitor systems numerous capacitors have been torn apart for failure analysis. The failures were due to excessive changes in capacitance, dissipation factor or leakage current on shelf or life test. A large part of these failures could be ascribed to reactions of the foil-electrolyte system, unaffected by trace contaminants or materials of construction. Analysis of these devices showed that in almost every case at least one of the following phenomena had taken place:

- 1. Increase in capacitance of the anode foil accompanied by decrease in ability to withstand voltage stress.
- 2. Increase in cathode foil capacitance.*
- 3. Production of gas.

For example, a set of 25,000µF, 10 volt capacitors were maintained at 10 volts and 85 C for 1000 hours. At that time the capacitance had increased about 17%, the dissipation factor had doubled and the leakage current had increased fourfold. During failure analysis these capacitors yielded a considerable amount of gas which ignited with a "pop", characteristic of hydrogen. The capacitance of the anode foil had increased 17%, which accounted for the increase in capacitance of the device. The increase in leakage current was due to the same degradation of dielectric which resulted in the capacitance increase. Such "leaky" oxide dielectrics also exhibit greater than normal dissipation factors.2 However, most of the observed increase in dissipation factor was probably due to replacement of electrolyte by gas within the capacitor windings, which increased the series resistance between anode and cathode foils.

Failures due to increase of anode foil capacitance become more evident as the voltage rating decreases. This is illustrated by some data on 3 voltand 5 volt devices that were tested at rated voltage for 2000 hours at 85 C. The ratios of final to initial parameter values were the following:

^{*}Aluminum which has not been anodized will have a thin "natural" oxide surface film and hence exhibit a large but finite capacitance.

	Capacitor		Anode Foil	
Rating	C/Co	DF/DFo	<u>c/c</u>	
3∨	1.23	3.12	1,66	
5V	0.97	2.09	1.10	

The large capacitance increase of the anode foil in the 3 volt unit was damped by the series capacitance effect of the cathode foil so that the net increase for the device was reduced.

Failures due to an increase of anode capacitance occur on shelf test as well as on life test. Some $75\mu F$, 5 volt non-polar capacitors were subjected to a severe shelf test of 500 hours at 105 C. The devices suffered a 14% capacitance increase which was accounted for by a similar increase in the foil capacitance.

Addition of water to the capacitor electrolyte usually reduces the dissipation factor and improves the low temperature characteristics. It also increases the attack of anode and cathode foil. Two sets of $100\mu F$, 5 volt capacitors, one containing 20% added water, were shelf tested for 340 hours at 105 C. The average parameter changes for the devices and the foil were the following:

	Device		Foil C/Co	
	C/Co	DF/DFo	Anode	Cathode
no added H ₂ O	1.00	1.54	1.03	1,22
20% added H ₂ O	0.82	20.9	4.32	0.71

The capacitors with no water added did not fail, though the cathode foil did exhibit a significant capacitance increase. The devices with water failed because of a very large increase in dissipation factor; and a decrease in capacitance which occurred despite a large increase in anode capacitance. This strange circumstance is explained by the fact that the capacitors were very gassy so that not only was electrolyte forced from the windings which increased the dissipation factor, but enough of the dielectric was insulated to reduce the effective capacitance. The decrease in cathode capacitance is unusual and perhaps is a specific effect associated with the added water.

In all of these examples, glycol-borate electrolytes were used in the capacitors. For many years these have been the electrolytes most commonly used in aluminum electrolytic capacitors. They are made by dissolving ammonium pentaborate in glycol or by dissolving boric acid in glycol and then bubbling ammonia through the solution or by some variation of these schemes. The final electrolyte is usually slightly basic.

Sometimes water is added to the system. Even without water added there is always a significant amount of water in these electrolytes, in the range 5-15%, because the borate ions and glycol react to form a glycol-borate ester anion and water.

II. EXPERIMENTAL PROCEDURE

The same type of capacitance increases as described above were obtained by placing a sample of anode or cathode foil in a jar of electrolyte and heating in an oven. Capacitance and weight changes of foil samples were measured as a function of time in the electrolyte; some observations on gas evolution were also made. Most of the work was without applied voltage though one experiment on the effect of applied voltage was performed. The foil used was commercial etched foil with a minimum purity of 99.97% aluminum. The anode foils had been anodized in hot aqueous 1 g/1 NH4H2PO4 at various constant voltages*. The electrolyte used was 17% ammonium pentaborate in glycol, a simple but representative system.

Electron micrographs were obtained of electropolished plain foil anodized to 10V and 40V and then exposed to the electrolyte. Anodization was in 1 g/1 NH₄H₂PO₄ at 90 C and a current density of $50\mu\text{A/cm}^2$ until the desired voltage was reached. This voltage was then maintained until the current density dropped to $4\mu\text{A/cm}^2$ for a 10V sample or $10\mu\text{A/cm}^2$ for a 40V sample. The following micrographs were obtained using the indicated sample preparation:

Mi	crograph Subject	Preparation
а.	Oxide film	Transmission through oxide film which had been removed from base metal with HgC12.
Ь.	Oxide/air surface	Carbon negative replica shadowed 15°.
c.	Aluminum at metal/oxide interface	Oxide dissolved in H ₃ PO ₄ - Cr ₀ 3 stripping solution ^{3†} . Carbon negative replica of metal surface shadowed 15°.
d.	Oxide at metal/oxide interface.	Plastic film laid down on oxide/ air surface. Oxide + plastic re- moved from metal as in (a). Ox- ide surface from metal-oxide in- terface then shadowed 15° and some carbon deposited for strength. Plastic film then dissolved.

[†]This treatment produced no discernible structure of its own on the metal surface.

*The dielectric thickness is proportional to the anodizing voltage, the constant being about 13A/V.

The most obvious feature of the results to be presented is that the rate of capacitance increase was far greater than any ever observed in a capacitor. The reasons for this difference warrant some comment before examination of these results. In these laboratory experiments the ratio of electrolyte volume to projected area of foil surface was about 3cc/cm². In a capacitor this ratio is of the magnitude 10-2 cc/cm2. In a capacitor the change in electrolyte composition due to reaction with the foil may not be negligible, as it is in a beaker. Depletion of reactant or build-up of product would decrease the reaction rate. Moreover, the geometry of a capacitor not only hinders the movement of fresh bulk electrolyte to the foil surface, but even the diffusion of ions or molecules is probably retarded by the fibrous paper matrix through which they must move. This may be the limiting factor which determines the rate of reaction, and hence capacitance change. An idea of the magnitude of these effects was obtained by comparing the capacitance increase of an etched 10V foil sandwiched between two similar foils held in place by glass microscope slides, with the increase of an identical sample exposed to bulk electrolyte. Both the sandwich and the exposed sample were immersed in the same jar of electrolyte and kept at 85 C for 142 hours. At that time the capacitance of the exposed foil had increased 190%; that of the foil in the sandwich had increased only 7%. There is no reason to believe that the mechanism of failure is any different in these two cases; however, it is important to realize that the results presented here are for a system that does not have the inhibiting properties of a commercial capacitor.

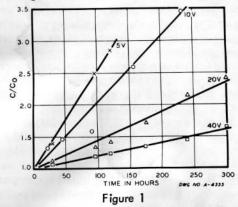
III. RESULTS

A. Capacitance and Weight Changes

The increase in capacitance of anodized etched foil immersed in glycol-borate electrolyte at 85 C is shown in Figure 1. It is apparent that the capacitance of foil anodized to low voltages is affected to a greater extent than that anodized to higher voltages. Since the capacitance is inversely proportional to the dielectric thickness, the rate of increase of reciprocal capacitance is a direct measure of the rate at which the average effective dielectric thickness decreases. In Figure 2 the data of Figure 1 were replotted in this fashion; it appears that the rate of dielectric degradation increases with initial oxide thickness. For any initial thickness the rate of degradation decreases with time.

When the weight change of foils immersed in 85 C electrolyte was measured a weight loss was observed in all cases. Some typical results are shown in Figure 3 for 10 volt and 40 volt foils. These weights are for 200 cm² surface area, i.e., 10cm x 10cm sample size. Results were

reproducible to ± 0.3 mg. The coincidence of the data for the two voltages indicates that the rate of attack is independent of film thickness. This contradicts the interpretation of the capacitance data in Figure 2.



CAPACITANCE INCREASE VS TIME IN ELECTROLYTE FOR FOUR OXIDE THICKNESSES

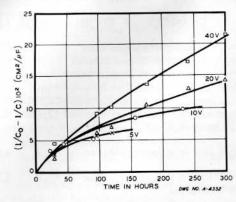


Figure 2

DECREASE IN DIELECTRIC THICKNESS AS MEASURED BY RECIPROCAL CAPACITANCE (Same Data as Figure 1)

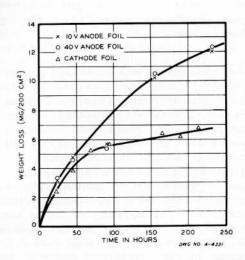


Figure 3

WEIGHT LOSS vs TIME IN ELECTROLYTE AT 85 C

After immersion in electrolyte for 232 hours the samples of Figure 3 were stripped of remaining oxide in H3PO4-CrO3 stripping solution. Eresh pieces of foil that had not been attacked by electrolyte were also stripped of oxide. These weight changes are listed in Table I. For both voltages the total weight loss in electrolyte and stripping solution (a + b) is greater than the initial weight of oxide (c). This difference is small and could be due to experimental error; however, the electron micrographs to be discussed shortly indicate that this difference is probably due to weight loss of the substrate aluminum during immersion in electrolyte. If the dissolution of oxide was uniform, the decrease in dielectric thickness determined from capacitance change would equal that calculated from weight change. This was the case for the 10 volt sample, but the comparison for the 40 volt samples indicates non-uniform attack of the dielectric.

Table I

WEIGHT CHANGES OF ETCHED ANODE FOIL

200 cm² sample area average of two samples all weights in milligrams

		10V	40V
(a)	Weight loss in electrolyte (232 hours at 85 C)	12.0	12.3
(b)	Weight loss in stripping solution	4.2	41.5
(c)	Weight loss in stripping solution (fresh samples)	15.2	53.5
	apparent metal weight loss (a + b - c)	1.0	0.3
	fraction of oxide dissolved $(1 - \frac{b}{c})$	0.724	0,225
	fraction of dielectric degraded (from capacitance)	0.720	0.317

When cathode foil was immersed in electrolyte at 85 Cthe capacitance increased to a limiting value within two hundred hours. Cathode foil suffers a weight loss upon exposure to electrolyte as shown in Figure 3. There is an important difference between the weight loss of this foil and of anode foil. As was done with anode foil, the oxide film was stripped from cathode foil by immersion in H3PO4-CrO3 solution. The weight of oxide on foil that had not been exposed to 85 C electrolyte was 1.2 mg/200 cm². The sample used for the data of Figure 3 had 2.5 mg of oxide after 213 hours exposure to electrolyte. Thus, immersion in the electrolyte resulted in the growth of a small amount of oxide. It is obvious that the amount of oxide present is insufficient to account for the weight loss in electrolyte which must be due to a net loss of metal. Since the capacitance increased despite the growth of oxide this new growth must be a poor dielectric.

When voltage is impressed across an electrolytic capacitor, a small leakage current is observed. To support this current, electrochemical reactions must occur at the anode and cathode to an extent equivalent to the current passed. The most likely reaction at the cathode is the production of hydrogen gas. This reaction could account for the build-up of gas observed during life test. Gas is also observed on shelf test and, to determine the site of this reaction, samples of anode and cathode foil were separately immersed in electrolyte in such a manner that any gas evolved would be collected. After ten days at 85 C, a sample of 10 volt anode foil had undergone a fourfold capacitance increase and a weight loss of 4.6 mg. No gas was apparent, though as little as .05 ml. could have been detected easily. Gas was collected over a sample of cathode foil; chromatographic analysis showed the presence of hydrogen. After one week, a quantity of gas equivalent to 0.25 milliequivalents of hydrogen had been collected while the foil weight loss was equivalent to 0.36 milliequivalents of aluminum. Since it is likely that some additional gas remained trapped within the foil etch structure, it would appear that to a first approximation the reaction between cathode foil and electrolyte can be explained by a dissolution of metal and evolution of hydrogen.

As mentioned previously, adding water to glycol-borate electrolytes increases the probability of capacitor failure. Ways to inhibit this effect have been proposed⁴. The effect of added water is clearly shown in Figure 4 to be an increased rate of degradation of anode dielectric and increased rate of reaction at the cathode.

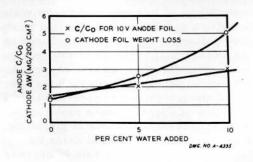


Figure 4

EFFECT OF WATER CONTENT ON THE RATE OF ELECTRODE REACTIONS

(Samples in electrolyte for 50 hours at 85 C)

To get some idea of the effect of applied voltage on the degradation of anode foil, samples of 10 volt foil were maintained at several voltages with respect to a platinized platinum cathode. After 96 hours at 85 C the capacitance increases recorded in Figure 5 were obtained. Results at zero potential were obtained by shorting the foil and platinum; the open circuit potential of the 10 volt foil varied between -.48 and -.51 volts vs. platinum. A small positive bias apparently increased the attack. At sufficiently high potential however, the rate of degradation decreased with increasing potential.

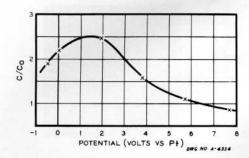


Figure 5

EFFECT OF APPLIED VOLTAGE ON THE CAPACITANCE INCREASE OF 10 VOLT ANODE FOIL

(Samples at constant voltage in electrolyte for 96 hours at 85 C)

B. Electron Micrographs

Samples of electropolished aluminum foil (99.99% purity) were subjected to the same treatment as the etched foils just discussed. The rate of attack of polished foil was less than that of etched foil. The different anodization procedures used (constant current vs constant voltage) may have contributed to this difference. Some comparative figures on the capacitance increase (C/Co) of these foils are the following:

	C/Co	
	Etched	Polished
10 Volt film 240 hours immersion	3.44	2.41
40 Volt film 340 hours immersion	1.67	1.48

Examination of these electropolished foils by optical microscopy showed nothing significant; however, electron microscopy revealed how the anode and cathode foils were attacked. Figure 6 shows the appearance of foil anodized to 10 volts. Both the oxide/air and metal/oxide surfaces appear quite smooth with no significant structure.

The oxide transmission micrographs showed no contrast except for an occasional imperfection such as the black area in Figure 6c. The oxide/ air surface of a 10 volt foil after immersion in electrolyte for 240 hours (Figure 7a) did not appear very different from the surface of anodized foil that had not been in electrolyte. However, the aluminum surface at the metal/oxide interface (Figure 7b), had undergone some pitting attack at grain boundaries and at points within grains. Transmission micrographs through the isolated oxide (Figure 7c) show a thickened oxide at grain boundaries and at points within the grain which correspond in size and distribution to the pits seen in Figure 7b. Anodized samples that had not been immersed in electrolyte sometimes showed slight grain boundary delineation but not to the extent found with samples after immersion. The "orange peel" structure observed throughout the oxide is a characteristic of electropolished foil5.

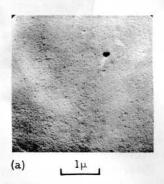
Micrographs of foil anodized to 40 volts and immersed in electrolyte for 340 hours are shown in Figure 8. Pits, as well as some grain boundary delineation are seen in the oxide at the oxide/ air interface. The metal surface exhibits severe pitting within grains and at boundaries. In addition to pits there appear to be small humps on the metal surface. Examination of several micrographs showing these structures led to the idea that they may be oxide particles not yet dissolved by the stripping solution. This oxide may possibly fill pits in the metal surface. Unlike the 10 volt film attacked by electrolyte, the transmission photo of the 40 volt oxide film showed numerous thin spots and holes in the oxide rather than a few thickened areas.

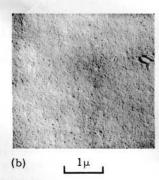
It was thought that the thickened grain boundaries and oxide nodules of the 10 volt film and postulated oxide-filled pits of the 40 volt film represented new oxide growth that occurred during immersion in electrolyte. If these new oxide particles were not sufficiently adherent to the surrounding anodic oxide they might drop off during sample preparation, perhaps leaving the holes seen in Figure 8c. The preparation of samples for observation of the oxide surface at the metal/ oxide interface was done most gently in order to minimize "fall-out"; the use of a plastic coating helped by keeping the oxide film more rigid. The result of this preparation is seen in Figure 8d. Nodules of oxide are in evidence as well as thin spots or holes. The shadows cast by the nodules show that they are at the metal/oxide interface, about .05 - . lu long and about the same diameter. The light spot in the center of each nodule could indicate a central channel, though the shadowing operation could have resulted in this appearance. The transmission micrograph in Figure 7c was obtained without shadowing and the nodules here

also show a light center, which supports the idea of a central channel.

It should be noted that in calculating the fraction of oxide dissolved in Table I, no consideration was given to this new oxide growth, i.e., it was assumed that the weight of new oxide was negligible compared to the weight of anodic oxide dissolved. If this was not the case, then the figures given for fraction of oxide dissolved are too low. Similarly, the weight of anodic oxide dissolved is greater than the observed weight loss in the electrolyte.

A sample of electropolished foil that had not been anodized was immersed in electrolyte for one week at 85 C. Figure 9a is a negative replica of this foil surface. It is very similar in appearance to anodized foil that has been in electrolyte (Figure 7a) except for the delineation at grain boundaries. The metal has been attacked (Figure 9b) in the same way as the metal substrate of anodized foil but to a greater extent. The oxide on this specimen was too thin to permit transmission micrographs.





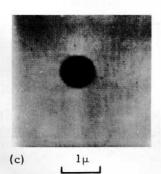
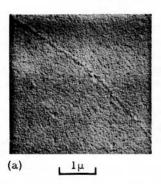
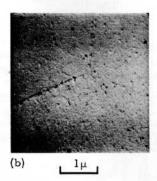


Figure 6

ELECTROPOLISHED ALUMINUM FOIL ANODIZED TO 10 VOLTS

- (a) Oxide/air surface; black spot is dust particle photographed to show shadow direction
- (b) Metal surface at metal/oxide interface
- (c) Transmission micrograph of oxide film; black area is a random imperfection





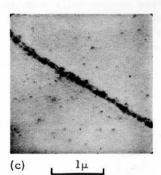


Figure 7

ELECTROPOLISHED ALUMINUM FOIL ANODIZED TO 10 VOLTS AND IMMERSED IN ELECTROLYTE FOR 240 HOURS AT 85 C

- (a) Oxide/air surface
- (b) Metal surface at metal/oxide interface; large black spots at top and bottom are dirt particles
- (c) Transmission micrograph of oxide film

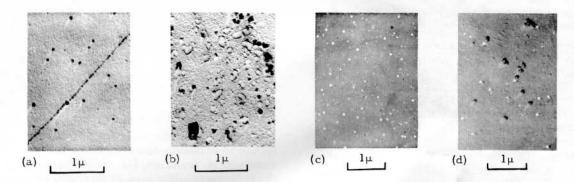


Figure 8

ELECTROPOLISHED ALUMINUM FOIL ANODIZED TO 40 VOLTS AND IMMERSED IN ELECTROLYTE FOR 340 HOURS AT 85 C

- (a) Oxide/air surface
 (b) Metal surface at metal/oxide interface
 (c) Transmission micrograph of oxide film
- (d) Oxide surface at metal/oxide interface

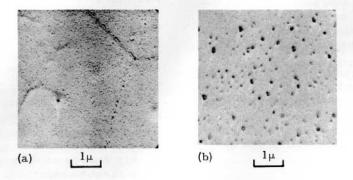


Figure 9

ELECTROPOLISHED ALUMINUM FOIL IMMERSED IN ELECTROLYTE FOR 168 HOURS AT 85 C NO PRIOR ANODIZATION

- (a) Oxide/air surface; wrinkles at left occurred during sample preparation
- (b) Metal at metal/oxide interface

IV. DISCUSSION

The capacitance increase of anode foil immersed in glycol-borate electrolyte was due to dissolution of the oxide dielectric. This occurred through a combination of uniform dissolution and attack concentrated at grain boundaries and at apparently random sites within a grain. At these points the substrate metal was also attacked, the corrosion product being a new growth of aluminum oxide. This new oxide grew to too great a thickness to be considered a barrier layer, i.e., it is not a good dielectric. The degree of non-uniform attack increased with increased initial oxide thickness. This may account for the increase rate of dielectric degradation with anodization voltage (Figure 2).

After attack by electrolyte, cathode foil had an appearance similar to that of anode foil, i.e., the metal was pitted and an oxide of poor dielectric properties had been formed. With cathode foil these phenomena were accompanied by evolution of hydrogen but not so with anode foil. It is probable that hydrogen was also produced on anode foil in these experiments but because of the much smaller quantities involved, it all remained adsorbed on the foil and dissolved in the electrolyte so no gaseous product was collected.

There is one set of reactions that fits equally well the observations with both anode and cathode foils. It was mentioned earlier that glycol-borate electrolyte is slightly alkaline and contains some water. In such an environment the dissolution of aluminum oxide probably proceeds via the overall reaction.

$$A1_2O_3 + 3H_2O + 2OH \longrightarrow 2A1 (OH)_4$$
 (1)

When the oxide has been thinned to its equilibrium thickness any further dissolution is accompanied by rapid production of new oxide to maintain the equilibrium barrier layer thickness. This would be an electrochemical process, the anodic reaction being the consumption of metal to form oxide and the cathodic reaction the evolution of hydrogen; i.e.,

anodic:
$$2 \text{ Al} + 3\text{H}_2\text{O} - 6\text{e} \longrightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+$$
 (2a)

cathodic:
$$2 \text{ H}^+ + 2e \longrightarrow H_2$$
 (2b)
or $2 \text{ H}_2\text{O} + 2e \longrightarrow H_2 + 2\text{OH}^-$

At steady state the dissolution of oxide would be just balanced by the formation of oxide. The net result would be dissolution of metal and production of hydrogen. At an anode, with its relatively thick oxide, the dominant reaction is dissolution of oxide. At only a few sites does the oxide become thin enough to support reaction (2a).

However, at a cathode the barrier oxide is soon thinned sufficiently so that reactions (2a) and (2b) can proceed over the entire surface. These reactions are sustained by the continuous dissolution of oxide. The new oxide growths on both anode and cathode foil were too thick to be all barrier film, but must consist of a thin barrier layer and a thicker conductive oxide.

For both anode and cathode foil the rate of attack is probably determined by the rate of the reaction in Equation (1). If H₂O is involved in the rate-controlling step of this overall reaction it is easy to see why increasing the water concentration increase the reaction rate (Figure 4). If only OH⁻ is involved in the rate-controlling step, the relationship with water is less obvious. However, one of the equilibria present in this electrolyte is,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
 (3)

Increasing the water concentration shifts this equilibrium to the right, increasing the OH⁻ concentration. In addition, as the water concentration increases, the dielectric constant of the solvent increases, which promotes further ionization shifting the equilibrium in Equation (3) further to the right. Thus, whatever the mechanism may be, if the reaction in Equation (1) is rate controlling, then higher water content will increase the attack.

No satisfactory interpretation of the results with applied voltage (Figure 5) can be offered. With a positive potential on the anode foil there was a tendency to form new oxide to repair the damage done by oxide dissolution. The net rate of attack can be expressed as $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, where \mathbf{r}_1 = rate of dissolution and \mathbf{r}_2 = rate of anodization. With a few volts positive potential \mathbf{r}_2 became significant, but not until about eight volts were applied did $\mathbf{r}_1 = \mathbf{r}_2$. It is not known why \mathbf{r}_1 increased with positive potential though this is perhaps the most significant characteristic of these data.

From this detailed description of the surface reactions that give rise to particular failure modes, it should be possible to devise systems of improved reliability in which these reactions proceed at a significantly slower rate. Indeed, systems have been developed and are in use in which the effect of these reactions is eliminated for all practical purposes. Unfortunately, much of the information in this area is of a proprietary nature but several examples may be cited.

Based on the proposed reaction mode, use of an electrolyte with a reduced water content should result in a more stable system. When an ammonium salt of a weak acid is dissolved in glycol, no water is produced via a chemical reaction as

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with glycol-borate electrolytes. The only water in this type of electrolyte is the small amount picked up during the manufacturing process. When a 10 volt foil was immersed in such an electrolyte at 85 C for 160 hours, the capacitance remained essentially unchanged, the initial value being $151\mu F$ and the final value $146\mu F$. No gas was evolved from cathode foil immersed in this electrolyte for a similar period of time.

Dimethylformamide is a solvent commonly used in electrolytes for foil tantalum electrolytic capacitors. With the choice of a suitable solute it can be used in aluminum systems at temperatures up to 125 C. Ten volt foil was immersed in such an electrolyte and kept at 125 C for 146 hours. The initial foil capacitance was $152\mu F$ and the final value was $153\mu F$.

The properties of anodic aluminum oxide depend on the conditions of anodization. Oxides more resistant to attack by glycol-borate electrolyte can be produced by proper choice of anodizing conditions. For example, from Figure 1 it is seen that foil anodized to ten volts at the conditions used for this study had a C/Co value of 2.57 after 150 hours at 85 C. In comparison, foil anodized in the same solution but at 25 C and constant current had a C/Co value of only 1.98 after the same exposure.

V. CONCLUSIONS

- Some of the parameter changes of aluminum electrolytic capacitors observed during life and shelf test are due to slow reactions between the electrodes and electrolyte.
- The capacitance increase of anodefoil immersedinglycol-borate electrolyte is the result of dissolution of the oxide dielectric. The net result of the reaction

between cathode foil and electrolyte is dissolution of aluminum and production of hydrogen.

- These reactions can be studied at an accelerated rate in the laboratory by the simple technique of eliminating the inhibiting geometry of a capacitor.
- 4. Modification of the electrolyte and/or oxide dielectric has produced systems in which these reactions proceed at a significantly slower rate. Systems are in use in which the effect of these reactions is essentially eliminated.

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