

Identification of Missing or Insufficient Electrolyte Constituents in Failed Aluminum Electrolytic Capacitors

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Introduction

Beginning in late 2001, a number of online newsgroups and industry publications started reporting the early failures of low effective series resistance (ESR) aluminum electrolytic capacitors manufactured in Taiwan. The most obvious characteristic of these failures was the bulging of the capacitor enclosure prior to loss of electrical function (see Figure 1). These capacitors had been produced in the millions under contract to multiple capacitor suppliers, and they had widespread use in the mass-produced electronic products of several companies, potentially causing the early failure of hundreds of thousands of end units.

While several articles describing the bulging and early failure of these capacitors were published in late 2002 and early 2003, the root cause of the failures was only speculated to be a missing component of their electrolyte [1-6]. Responding to the request of a capacitor supplier, the CALCE Electronic Products and Systems Center (EPSC) undertook an extensive study of 1000 microfarad, 10 volt, aluminum electrolytic capacitors susceptible to bulging and early failure.

Initial Chemical Properties

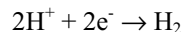
The initial effort was to establish cause of the case bulging. Based on an understanding of electrolyte chemistry and knowledge of similar failures from older generations of electrolytic capacitors, it was speculated that hydrogen evolution was initiating the increase in internal pressure. Mass spectroscopy of gas emanating from several punctured bulged capacitors confirmed this hypothesis (see Figure 2).

To prevent hydrogen gas formation, proprietary depolarizers are often added to the electrolytic solution to react with hydrogen atoms that would otherwise bond to each other, forming molecules of gas.

Depolarizers, also known as degassing agents or getters, are often nitro-substituted aromatic compounds (nitroaromatics), sorbate compounds, amine salts, or soluble inorganic salts. The amount of depolarizer necessary to prevent gas formation depends on the chemical being used. Nitroaromatics are typically added in amounts of approximately 1 wt%. Sorbic acid has been used in amounts ranging from about 0.1 wt% to 15 wt%, but it seems to be most optimal in concentrations of 2 wt% to 3 wt%. Inorganic salts are used over a range from around 0.1 wt% to 5 wt%.

A review of ion chromatographic and mass spectrographic analyses of capacitor electrolytes did not yield an obvious depolarizer (ion chromatography can detect ions down to 0.1 ppm while mass spectroscopy is sensitive to approximately 10 ppm).

The presence of impurities in the aluminum foil can also induce gas generation. Metals such as copper, magnesium, iron, and zinc, can form galvanic couples with aluminum. These create electrons that might combine with hydrogen ions in the electrolyte solution in the reaction



to produce gaseous hydrogen. Such production would only occur at the cathodic plate, as the anodic plate is covered by the dielectric. A patent by R. Dapo of the Philips Corporation [7] suggests that the purity of the aluminum foil should be greater than 98 wt%.

To see if the excessive hydrogen was being produced by impurities in the capacitor foil, wavelength dispersive x-ray spectrographic (WDS) analyses of foils from a capacitor from the lot of Taiwanese capacitors known to bulge and foils from a capacitor from a lot of non-bulging Japanese capacitors were

performed. A small amount of magnesium was detected in both the Taiwanese and Japanese foils, and copper was detected in the Taiwanese foils alone (see Table 1). Ignoring the topical constituents of oxygen and carbon, the purity of the cathodic aluminum foil from the Japanese capacitor worked out to be approximately 99.1 wt%, which was within the limit set by Dapo. The purity of the cathodic aluminum foil from the Taiwanese capacitor was approximately 97.5%, which was below the minimum value stated by Dapo. The insufficient purity of the Taiwanese aluminum foil could cause gaseous hydrogen production that would not be impeded by a depolarizer, but the galvanic couples were not thought to be sufficient to account for the rapid production of hydrogen gas that was necessary to cause the relatively rapid bulging of the capacitor cans.

There were other anomalies in the ion chromatographic analyses, chiefly variations in the amounts of ammonium and phosphate ions present. Ammonium ions in water form ammonium hydroxide, which is strongly basic. This raised concerns about the pH of the electrolyte in the bulging capacitors, as a review of the chemical properties of aluminum oxide – the dielectric – showed that it is slightly soluble in basic solutions (but not in acidic)[8]. Measuring the pH of electrolytes from capacitors from the Taiwanese lot known to bulge and from a Japanese lot that had not exhibited bulging showed that the electrolytes of the bulging lot were weakly basic ($7 < \text{pH} < 8$), while those of the non-bulging lot were acidic ($\text{pH} \approx 4$).

Initial Electrical Investigation

Parametric measurements were performed on capacitors retrieved from the field. Review of results showed that some of the capacitors exhibited a rising capacitance prior to bulging. Normally, due to loss of electrolyte through the base plug seal, electrolytic capacitors have a slightly decreasing capacitance until a rapid falloff occurs at the end of life. It was possible to explain the anomalous behavior as the result of dielectric thinning, which could be due to dielectric dissolution in the basic electrolyte.

Electrical Testing

Electrolytic capacitors from a lot known to be susceptible to bulging were subjected accelerated stress testing at 55°C with a bias of 3.3 volts (the application voltage). Capacitance, ESR, and leakage current were periodically measured at room

temperature. The capacitance was found to increase slowly up to 1100 microfarads, at which point the rate of capacitance rise increased significantly and leakage current exceeded manufacturer's specifications. This trend continued until seal breakage and electrolyte loss, at which point capacitance and leakage current plummeted and ESR increased (see Figures 4, 5, and 6).

This is in contrast to the behavior seen with capacitors from a different lot and capacitors from a Japanese manufacturer. Both capacitor sets displayed the more common degradation of a gradual decrease in capacitance.

Chemical Testing

Electrolyte samples from the suspect lot of Taiwanese capacitors, a different lot of Taiwanese capacitors not exhibiting bulging, and a lot of capacitors from two Japanese manufacturers were subjected to additional pH and ion chromatographic testing (see Table 2). Both Taiwanese samples were slightly basic, while both Japanese samples were acidic. Increased pH was most likely due to the presence of ammonium ions, which are present only in the electrolyte from the Taiwanese samples. The Taiwanese sample from the bulging lot did not contain significant amounts of phosphate ions, while that from the non-bulging lot did. Similar results were seen with the electrolyte from the Japanese manufacturers, with phosphate ions present in one sample and absent from the other. Review of the chemical properties of aluminum phosphate showed that it is not soluble in basic solutions [8], making it a candidate for a protective coating on aluminum oxide in the presence of a basic electrolyte.

Suspecting that unprotected aluminum oxide dielectrics were dissolving into the alkaline electrolytes, energy dispersive spectroscopy (EDS) was performed on evaporated electrolyte from the capacitor samples described previously. The electrolyte from the lot of Taiwanese capacitors exhibiting bulging contained aluminum; aluminum was not detected in the electrolyte from the other capacitor samples (see Figure 6).

Discussion

The hypothesized root-cause of failure, insufficient balance of pH and phosphate levels, has been validated through the measurement of electrical

behavior of capacitors retrieved from the field. Capacitors were found to have elevated levels of capacitance, which is an indication of thinning of the dielectric layer. Thinning of the dielectric layer is most likely due to dissolution of aluminum oxide into the electrolyte. Dissolution in electrolytic capacitors occurs when the concentration of phosphate is insufficient in relation to the pH of the electrolyte chemistry.

It is important to note that the capacitors under investigation had been tested by manufacturer to the specified lifetime at maximum rated voltage at maximum rated temperature. All electrical parameters were found to be within specification at the completion of this industry standard test. The reason for this experience is that the high voltage required for this test most likely sufficiently retarded dielectric dissolution until a time beyond the rated lifetime of these capacitors.

This experience points out a hazard of testing to specifications, instead of testing to failure. The industry standard test is based upon an expected failure mechanism – electrolyte evaporation. If an unexpected failure mechanism is introduced due to changes in material or architecture, the assumed acceleration factor may no longer be valid. A best practice approach is to test to failure, which is CALCE's recommended testing regime for electronic parts. If the manufacturer had tested to failure, it is likely that bulging would have been seen

near the end of life, and this would have indicated the existence of an unexpected failure mechanism.

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WDS X-RAY SPECTRA OF FOILS				
Taiwanese Bulging				
	Inner Foil (anode)		Outer Foil (cathode)	
	Atomic %	Weight %	Atomic %	Weight %
Aluminum	57.34	67.67	86.44	90.78
Oxygen	33.25	23.27	8.41	5.23
Carbon	5.52	2.90	3.65	1.71
Calcium	1.00	1.75	0.46	0.72
Phosphorous	2.29	3.10	0.60	0.73
Magnesium	0.23	0.25	0.17	0.16
Copper	0.38	1.06	0.27	0.67
Japanese Non-Bulging				
	Inner Foil (anode)		Outer Foil (cathode)	
	Atomic %	Weight %	Atomic %	Weight %
Aluminum	50.76	62.86	84.63	90.60
Oxygen	39.32	28.88	9.94	6.31
Carbon	7.63	4.21	4.74	2.26
Calcium	1.99	3.65	0.08	0.09
Phosphorous	0.22	0.31	0.58	0.71
Magnesium	0.08	0.09	0.04	0.04
Copper	-----	-----	-----	-----

Table 1: Wavelength dispersive X-ray spectrographic analyses of the foils of a Taiwanese bulging 1000 microfarad, 10 volt, aluminum electrolytic capacitor and the foils of a Japanese non-bulging 1000 microfarad, 10 volt, aluminum electrolytic capacitor.

Rated Capacitance	Rated Voltage	Origin	Bulging Status	pH	NH ₄	PO ₄
1000 μF	10 V	Taiwan	Yes	> 7	Yes	No
1000 μF	10 V	Taiwan	No	> 7	Yes	Yes
1000 μF	10 V	Japan	No	~ 4	No	Yes
1000 μF	10 V	Japan	No	~ 4	No	No

Table 2: Ion chromatographic and pH analyses of Taiwanese and Japanese capacitors.



Figure 1: A bulged 1000 microfarad, 10 volt, aluminum electrolytic capacitor manufactured in Taiwan in 2002. The photograph has been retouched to obliterate manufacturer identity information.

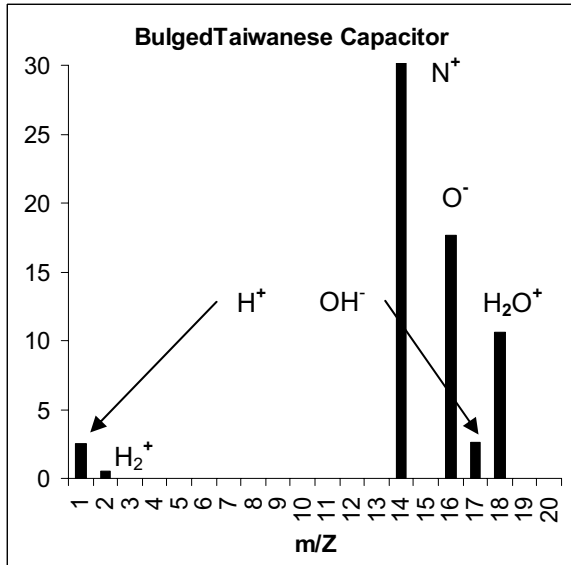


Figure 2: Mass spectrograph of the gas from a Taiwanese 1000 microfarad, 10 volt, aluminum electrolytic capacitor that had just started to bulge.

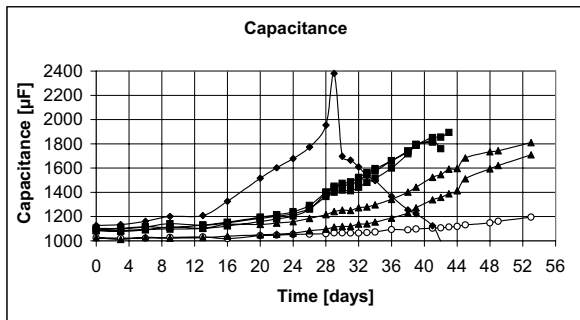


Figure 3: Capacitances of capacitors from the bulging Taiwanese lot tested at 55°C at a bias of 3.3 volts. Diamonds indicate the earliest failure, which has complete data. Squares indicate the second group of failures; data collection for these was terminated after they blew their cans off. Triangles indicate the third group of failures, which had just started to bulge. Circles indicate a capacitor just starting to produce a significant quantity of gaseous hydrogen.

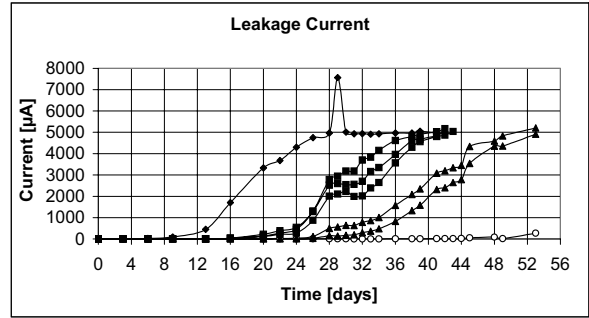


Figure 4: Leakage current of capacitors from the bulging Taiwanese lot tested at 55°C at a bias of 3.3 volts. Diamonds indicate the earliest failure, which has complete data. Squares indicate the second group of failures; data collection for these was terminated after they blew their cans off. Triangles indicate the third group of failures, which had just started to bulge. Circles indicate a capacitor just starting to produce a significant quantity of gaseous hydrogen.

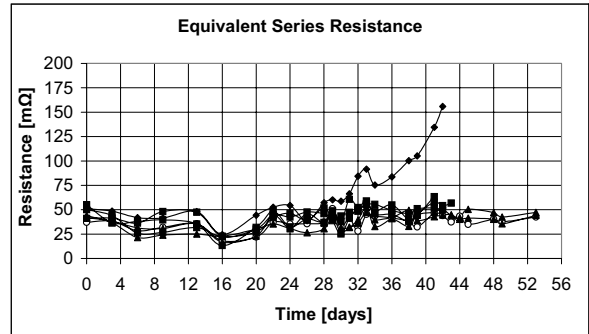


Figure 5: Equivalent series resistance of capacitors from the bulging Taiwanese lot tested at 55°C at a bias of 3.3 volts. Diamonds indicate the earliest failure, which has complete data. Squares indicate the second group of failures; data collection for these was terminated after they blew their cans off. Triangles indicate the third group of failures, which had just started to bulge. Circles indicate a capacitor just starting to produce a significant quantity of gaseous hydrogen.

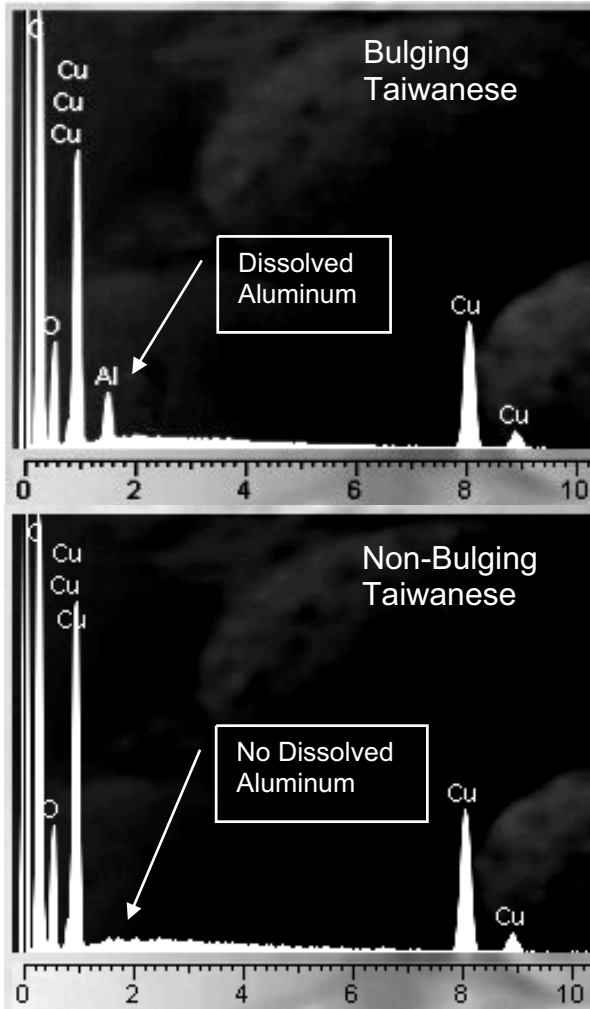


Figure 6: Energy dispersive X-ray spectrographic analyses of electrolyte samples from the Taiwanese capacitors exhibiting bulging and the Taiwanese capacitors not exhibiting bulging.