Support Note
Afraid of aging?
The effects of time on electrolytic capacitors

SN019 // FRANK PUHANE

1 Introduction

Since the development and production of electrolytic capacitors, designers have had to deal with the issues of aging and shelf life of these products. Electrolytic capacitors have been around for a very long time, but the rapid increase did not occur until the 1960s. There are still many "myths" from that time that revolve around the aging and shelf life of these capacitors. The main problem of that time was the materials available, which had a much lower quality standard than the materials used today. Aging is distinguished between the following changes in the capacitor performance: Change in capacitance, ESR and leakage current during operation (with voltage applied) and reduction of dielectric strength due to degradation of the dielectric (no voltage applied). There is also a guideline from the ZVEI on the long-term storage capability of components: During storage of an aluminum electrolytic capacitor, two different effects can adversely affect the blocking (insulation) capability of the capacitor, oxide degeneration and post-impregnation effects. If voltage is applied to the capacitor after a longer storage time, this can initially cause an increased regeneration leakage current. Shortly after a DC voltage is applied, the leakage current is relatively high and asymptotically decreases to a low leakage current after some minutes. After the aluminum electrolytic capacitors have been mounted on the printed circuit board, the increased leakage currents must be taken into account, e.g. in the first startup of the device, and the electrolytic capacitor must be given time to regenerate. If these effects cannot be compensated, the electrolytic capacitor must be reformed before assembly. [1] Forming is a special process to oxidize the anode electrode (i.e. aluminum oxide). However, why do these effects occur? These and other questions will addressed in this document.

2 Background Information

Due to the polar or non-symmetrical structure of an electrolytic capacitor, the electrodes are divided into anode and cathode. In an electrolytic capacitor, the anode consists of a processed metal foil and the conductive electrolyte forms the actual cathode. An oxide layer on the metal foil of the anode is used as the dielectric (insulation) between the two conductive electrodes. This oxide layer insulates the electrodes from each other. The thickness of this oxide layer changes repeatedly during the production process and during storage without voltage. It constantly decreases. This increases the leakage current of the capacitor. Electrolytic capacitors are differentiated in their construction based on two essential criteria. These are the electrode material used (such as tantalum or niobium) and the property of the electrolyte. The electrolyte can be liquid or solid. By specifying the relative permittivity of the different dielectrics, it is clear that the capacitance achieved per volume depends strongly on the dielectric used. This shows Figure 1.

The aluminum electrolytic and aluminum polymer capacitor are wound capacitors. The terminal pins bonded to the respective metal foil by a special process. The paper layer shown in Figure 2, which also referred to as the separator, finally completely impregnated with the electrolyte and in addition to storing the electrolyte, has the function of physically separating the metal foils, electrically insulating them and protecting them from damage. The electrode foil is often mistaken for the cathode, but the electrode foil only provides the electrical connection to the actual cathode, the electrolyte.

A special electrochemical process called forming creates the oxide layer. In this process, the oxide layer is created by applying the so-called forming voltage. The stronger the oxide layer is, the higher the voltage that can handled by this layer. After this process, a very slow degradation of this oxide layer begins if no voltage is applied. The longer the capacitor is voltage-free, the thinner the oxide layer becomes and consequently the dielectric strength decreases. This results also in an increase of the leakage current. As soon as voltage is applied again, the oxide layer is rebuilt, the leakage current decreases and the dielectric strength returns to the normal level. However, never as after the initial production. The forming voltage can be up to 30% higher than the actual nominal voltage of the capacitor. This means that the oxide layer is also up to 30% thicker. The resulting thickness of the oxide layer is proportional to the applied voltage (Figure 3: Aluminum foil with oxide layer). The anode foil is either rougher or smoother, depending on the intended use.

![Diagram of electrolytic capacitor](image-url)
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2.1 What happens during operation with applied voltage?
Electrolytic capacitors are used everywhere in electronics. Due to the applied voltage a certain temperature profile will be established at the capacitor, with a higher temperature in the core of the element and respectively lower on the surface. Several aspects, the heat generated by components as well as the heat from the surrounding, influence the ambient temperature. Other factors such as ripple current and frequency also play a role in calculating the expected life. The simple relationship between expected life and operating temperature is defined by the Arrhenius equation.

\[ L_x = L_{nom} \cdot 2^{\frac{T_0 - T_A}{10}} \]  

(1)

with \( L_{nom} \) = defined endurance, \( T_0 \) = upper temperature limit, \( T_A \) = application temperature.

Depending on the conditions under which the capacitor is operated, the amount of electrolyte is reduced by self-healing of the oxide layer (e.g. damage due to overvoltage), dry out or by diffusion through the sealing rubber.

2.2 What happens during voltage-free storage?
The storage conditions of electrolytic capacitors are defined in the data sheet. These conditions are temperature between 5 °C and 35 °C with a humidity between 10% and 75%. The quality of the oxide layer can deteriorate during storage without externally applied voltage, especially at higher temperatures. Since in this case there is no leakage current and as a result, the oxide layer will not regenerate. This leads to a higher leakage current flow when a voltage applied after prolonged storage. If a capacitor is exposed to high humidity for a long period, this can cause discoloration of the terminals (i.e. oxidation) and lead to poor solderability. The average storage conditions at Würth Elektronik are temperature = 22.48 °C and humidity = 37.51%. The storage capability of the capacitor is defined by the so-called shelf life. Please see Table 1 for information that is more detailed. The shelf life simulates the aging of the capacitor under the influence of temperature without an electrical load (voltage, current). The electrical parameters of the capacitor subsequently measured again after formation and at a room temperature of 20 °C.

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Endurance</th>
<th>Shelf Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifetime</td>
<td>2000 h @ 85°C</td>
<td>1000h @ 85°C</td>
</tr>
<tr>
<td>Voltage</td>
<td>Un-applied</td>
<td>none</td>
</tr>
<tr>
<td>Current</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>ΔC</td>
<td>≤ ± 25% of initial measured value</td>
<td>≤ ± 25% of initial measured value</td>
</tr>
<tr>
<td>DF</td>
<td>≤ 200% of the initial specified value</td>
<td>≤ 200% of the initial specified value</td>
</tr>
<tr>
<td>Leakage Current</td>
<td>≤ the initial specified value</td>
<td>Pre-treatment for measurements shall be conducted after application of DC working voltage for 30 min</td>
</tr>
</tbody>
</table>

Table 1: Example test conditions for Endurance and Shelf Life for SMD electrolytic capacitors

2.3 What is oxide degeneration?
The ZVEI guide describes oxide degradation as follows: Depending on the electrolyte class and temperature, ionic components of the electrolyte can diffuse into the dielectric or oxide and change the oxide crystal structure. Electrical defects and ionic charge carriers are formed in the oxide. Electrolytes based on the solvent glycol have an increased leakage current. The advantage of this electrolyte is its ability to repair defects in the oxide layer when current flows through the capacitor. As a result, these electrolytes are mainly used in high-voltage aluminum electrolytic capacitors. In the low-voltage range, the oxide layer is more homogeneous, so electrolytes containing the solvent gamma-butyrolactone are used here. This solvent produces a reliable and voltage-resistant oxide layer. An advantage of gamma-butyrolactone is that this solvent almost incapable of penetrate the oxide layer. As a result, a long voltage-free storage can be achieved, since the oxide layer is still well insulating even after a long time. If a measurement of the leakage current shows temporarily increased values after a long period of voltage-free storage, this is due to the post-impregnation effects.

2.4 What are post impregnation effects?
The ZVEI guide describes the post-impregnation effects as follows: The oxide can only be electrochemically formed in the component where it is also covered with electrolyte and electrically connected to the cathode foil via the electrolyte. This means that the necessary forming current can flow at these points. This is the case in a new capacitor for more than 99.9% of the oxide area to be formed. In the case of low-voltage aluminum electrolytic capacitors with solvent electrolytes such as gamma-butyrolactone, it is assumed that the oxide layer has formed in all areas of the anode foil in accordance with the applied forming voltage and has not degraded by the time the capacitor is used for the first time. It is therefore
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expected that these capacitors will have a very low leakage current. In principle, the post-impregnation effects also occur with high-voltage aluminum electrolytic capacitors, but they are negligible because the effects of oxide degradation are dominant. Nevertheless, forming can be an advantage, since forming makes the oxide layer more stable and thus reduces the resulting leakage current (albeit minimal).

3 Countermeasures and measurements

Ethylene glycol and gamma-butyrolactone electrolytes are used in Würth Elektronik products. These have different properties. Due to the fact, that the thickness of the oxide layer change by time, a longer storage without voltage can increase the capacitance and reduce the ESR. The leakage current provides a reliable basis for determining the condition of the oxide layer. By applying the nominal voltage via a 10 kΩ resistor, the oxide layer of the dielectric stabilizes; the dielectric strength and the leakage current stabilize to the initial level. The leakage current decreases after applying a voltage. In the data sheet, leakage currents given are after typically 120 seconds. Diagram 1 shows the leakage current over 2 min. with applied nominal voltage (U_R = 10 V_DC and I_{Leakmax} = 100 µA after 2 min.)

Furthermore, Würth Elektronik has established the so-called "Electrical Property Check" to check the electrical parameters of electrolytic capacitors. Data available on request. To show how the properties of the capacitors change over time, we measured the electrical properties of an aluminum electrolytic and aluminum polymer capacitor after five years of storage. Figure 5, 6 and 7 shows the measurement results for the aluminum electrolytic capacitor and Figure 8, 9 and 10 shows the measurement result for the aluminum polymer capacitor.
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Another point that influences the shelf life is the solderability of the components. A longer storage time can change the wettability of the solder connections and have an influence on the process ability of the components. All aspects described in this document describe physical effects as they occur to any capacitor of the respective technology. This information is for general information and does not represent a data sheet extension.

4 Conclusion

Capacitors, similar to many other components have a certain lifetime with a changing performance over the time. The change in the performance is very much dependent of the quality of the material used, the storage conditions before used in an application and the position on the PCB. The placement of the component can influence the entire expected lifetime of the application. The temperature on the surface and in the core of the component largely defines the lifetime. This temperature can rise above the defined temperatures in the application due to a hotspot or it can be kept at a defined level through active cooling. More information about aluminum electrolytic and aluminum polymer capacitors can be found in Application Note ANP071. More information specifically on the topic of expected lifetime can be found in Support Note SN008. By proper handling and adherence to the specifications defined in the data sheet, the electrolytic capacitor can be a reliable and long-lasting component. The loss of capacitance and the increase of the ESR during operation is compensated by a well thought-out dimensioning of the component. Prolonged voltage-free storage is also possible. Regardless of whether the capacitors are stored in their original packaging or already mounted, the degradation of the oxide layer and the resulting reduction in the maximum voltage that the capacitor can dissipate must be taken into account. The increased leakage current at the moment of switch-on must be tolerated by the application so that a frictionless start is possible. An upstream formation of the capacitors is also possible. The data sheet provides a detailed description of this.
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A Appendix

A.1 Literature

(1) ZVEI Leitfaden Langzeitlagerfähigkeit von Bauelementen, Baugruppen und Geräten

Leitfaden Langzeitlagerfähigkeit von Bauelementen, Baugruppen und Geräten (zvei.org)
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