Metallized Films for Capacitor Applications

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ABSTRACT

Metallized capacitor film technology has undergone a series of changes over the last ten to fifteen years in metallized electrode materials and metallizing equipment. Metallized aluminum electrodes for AC capacitor applications have been replaced by zinc based electrode systems, due to a high field electrochemical corrosion of thin aluminum electrodes. This change dictated new metallizing equipment capable of depositing electrode systems such Al/Zn alloys and multilayers of Al/Zn, Ag/Zn, Cu/Zn, and Ag/Zn/Al. The new electrode materials allowed the use of thin metallization or higher resistivity electrodes in the active capacitor region, for improved self healing properties, and thicker metallization or lower resistivity electrodes at the termination region, to facilitate current conduction. Metallizing machines were build that can deposit variable thickness metal in the machine direction. Driven by capacitor product needs, electrode demetallizing systems have been developed that are capable of producing high resolution patterns without compromising web speed and machine productivity. Lower voltage DC capacitor applications and the development of thin gage PET films has led to the development of metallizing machines that are capable of metallizing films as thin as 1.0µm PET at speeds in excess of 10m/sec. Continuing demands on capacitor product performance are leading to additional metallized film improvements such as plasma treatment, oil overcoats and polymer coatings, performed in the vacuum chamber in-line with the electrode metallization process.

BASICS OF METALLIZED CAPACITOR TECHNOLOGY

Metallized capacitors represent a large segment of the film-paper capacitor market which includes various liquid impregnated film-paper-foil designs as well as dry and impregnated metallized film and metallized paper designs. Capacitors with metallized electrodes can be dry or liquid impregnated, depending on the application conditions and the specification requirements. The metallized electrodes consist of a thin layer of aluminum or zinc based metal, that has a thickness of about 100-300Å and it is vapor deposited directly on the film or paper dielectric. Alternatively as shown in Figure 1, metallized electrodes can also be formed by metallizing both sides of a film or paper sheet, which is then used as an electrode with an unmetallized polymer film to produce a capacitor.

When compared to foil electrode capacitors, the major advantages of metallized capacitors include lower weight, in some cases lower volume, and higher reliability in low voltage applications, resulting from the “self healing” or “clearing” ability of the metallized electrodes. The terms self healing and clearing are used interchangeably, to describe a process in which the thin metallized electrode melts back in the event of a short, to isolate the failure site. Although the actual performance characteristics of different metallized capacitors depend on the particular polymer-electrode system and application conditions, certain features and failure mechanisms are common to most metallized capacitors. Aging and failure mechanisms that relate to the metallization process include the “self healing” or “clearing” property of the metallized electrodes, along with capacitance loss due to electrode corrosion.

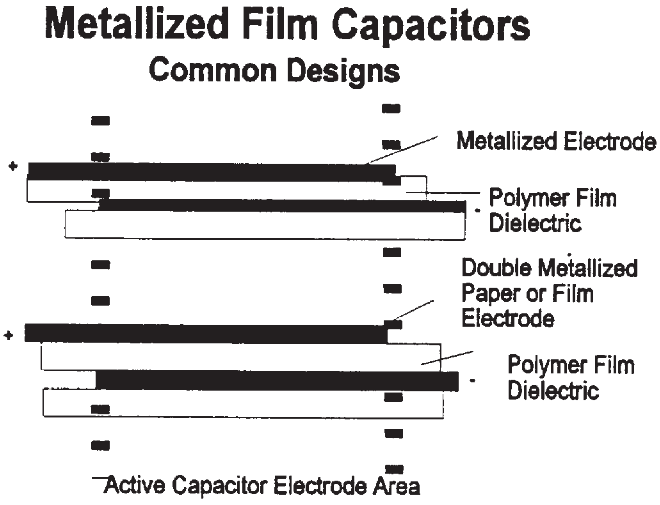

Figure 1. Schematic representation of basic metallized capacitor design configurations, showing the polymer dielectric and the metallized electrodes.

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Self Healing Property

Defects such as imbedded foreign particles or microflaws in the capacitor dielectric can result in weak spots that can lead to localized breakdowns of the polymer film. The breakdown event results in an arc between the two metallized electrodes that transiently discharges a portion of the stored energy. This generates a localized build up of temperature and pressure, which leads to vaporization of the polymer film (in the form of a small hole) and also vaporization and melt-back of the metallized electrode. The melt-back of the electrodes around the arc causes it to extinguish, which electrically isolates the two electrodes, preventing large-scale damage and total failure of the capacitor. This self healing event which is also referred to as a clearing, is instrumental in increasing the level of reliability in metallized capacitors. [1]

The ability of a metallized capacitor to self heal is based on several parameters. Key parameter that relate to the metallization process include the following:

1. Thickness and purity of the metallized electrodes: The thermodynamics of the self healing process combined with the requirement for low resistance in series with a capacitor, dictate an electrode material that has low melting point and high conductivity at low electrode thicknesses. These requirements limit the choices, for effective and low cost electrodes, to aluminum and zinc metals. The selection between aluminum and zinc is based on the application conditions. Aluminum electrodes are characterized by their resistance to environmental corrosion and are preferred for use in DC and many AC applications. However, aluminum is also subject to a rather unique corrosion mechanism that occurs only under AC voltage conditions [2]. As a result, zinc electrodes which have lower resistance to environmental corrosion than aluminum, are used in metallized capacitors for AC voltage applications.

In applications where the electrodes are protected from corrosion, it is desirable to have a thinner electrode. The energy of the clearing is proportional to the square of the thickness [1]. The thickness of the aluminum electrodes is usually specified by measuring the resistivity of the electrodes in ohm/square, which increases sharply as the thickness drops below about 100Å. This effect broadens the range by which one can specify the resistivity of very thin aluminum films.

2. Deposition rate: The thickness/resistivity relationship is also a function of the rate by which the aluminum is deposited on the polymer film [1]. At low deposition rates, the nucleation rate on the polymer substrate is low and the aluminum crystals grow large. At a vacuum level of 10^{-4} to 10^{-5} torr, the grains have time to oxidize and thus the boundaries can be somewhat contaminated. Both of these factors lead to higher values of resistivity for a given electrode thickness. Alternatively, if the resistivity is the only parameter that is specified and measured, films deposited at lower deposition rates will be thicker and therefore less clearable.

3. Purity of aluminum metal: Unlike aluminum metallization for packaging applications, high purity (99.99%) aluminum wire should be used for capacitor electrodes. The reason for this is that 99.9% pure aluminum when in the form of thin films it has lower conductivity at a given thickness and significantly worse corrosion resistance.

4.Surface functionalization of the polymer dielectric: The physical and chemical properties of the metallized electrodes are to a great effect affected by the quality of the surface of the polymer dielectric. Surface functionalization improves the nucleation, crystal structure and physical adhesion of the metallized electrode to the polymer film substrate. Advance methods of functionalizing the polymer film dielectrics include plasma treatment and polymer coating in the metallizer prior to the deposition of the metal electrode.

Capacitance Loss

Most metallized film capacitor specifications regard a 3% drop in capacitance, under accelerated life test, as a capacitor failure. This change in capacitance is an arbitrary point of reference for comparison of the relative performance of metallized film capacitors. Capacitance stability is therefore an important consideration in assessing the quality of the metallized electrodes.

The corrosion of the metallized electrodes is one of the predominant mechanisms of capacitance loss in a metallized capacitor. The chemistry of the aluminum and zinc electrodes in metallized capacitors is somewhat complicated by the variability in the purity and structure of the vapor deposited layers, and by the large surface to volume ratio that exists in a metallized electrode. The latter factor makes the corrosion rate particularly sensitive to the type of film and surface treatment. For example two polypropylene films produced by two different manufacturers can have different electrode corrosion rates when metallized side by side. Although metallizing film manufacturers are constantly facing a multitude of corrosion related issues, there are two dominant corrosion mechanisms. Namely AC electrode corrosion and environmental corrosion.

AC Voltage corrosion

AC voltage corrosion of aluminum electrodes is a rather unique phenomenon that is rarely observed in other electrical components. Unlike other corrosion mechanisms, the corrosion sites on the aluminum electrodes are in many cases perfectly circular, and they have been shown to be affected by several parameters, that include the properties of the base film, the frequency of the applied voltage and the voltage level [2]. Thinner aluminum electrodes, which are attractive due to their better self healing properties, cannot be used in

AC applications because of their higher corrosion rates. Although the aluminum oxide is one of the toughest and most stable oxides, its stability is effective over a narrow region of PH. It has been suggested that hydrolyzed moisture in the capacitor windings, when exposed to a positive and a negative voltage cycle, shifts the PH in the immediate vicinity of the electrodes to higher values [2]. While the voltage is applied on the capacitor, small amounts of adsorbed moisture on the electrodes, and absorbed moisture in the film, hydrolyze to produce H^+ and OH_- ions. During the positive cycle the protons move away from the oxidized metal surface, while the OH^- moves towards it causing a PH shift in the base direction. During the negative cycle, the n-type aluminum oxide conducts electrons to the attracted H^+ and hydrogen gas is liberated ($2H^+ + 2e^- = H_2$). The depletion of the protons in the vicinity of the electrodes increases further the OH^- concentration. The high PH values lead to the corrosion of aluminum via a dilution of the protective aluminum oxide.

$$Al_2O_3 + 2\ OH^- \leftrightarrow 2\ AlO_2^- + H_2O$$

Therefore, during the negative cycle, the original oxide is destroyed and more flaws are created. Some of the flaws may be healed by the positive cycle but the overall effect will be continuous corrosion. It has been shown that the corrosion of the aluminum electrodes is driven by the high fields that are created at the edge of an electrode or in a flaw anywhere in the electrode area. The high electrostatic fields can be better understood if one considers a semi-infinite thin electrode in parallel with an infinite electrode. At the exposed edge of the semi-infinite electrode, the field is very high due to the high non-uniformity. If aluminum oxide is added to the edge of the electrode, the field will be somewhat modified due to the different dielectric constant of the Al_2O_3, but it will remain very high. If a corrosion site initiates in some flaw in the metallization in the middle of an electrode, it will continue to grow equally in all directions, driven by the very high electric field. If the aluminum oxide was not such a good insulator and the field at the edge of the electrode was reduced then the oxide would cease to grow.

Environmental Corrosion

Some capacitor manufacturers avoid the use of aluminum in many AC capacitor applications in order to eliminate the AC corrosion problem. The alternative to aluminum is zinc electrodes, which do not undergo AC corrosion due to the semi-conducting nature of the zinc oxide. However, this approach is not free of problems. Unlike aluminum, zinc is not as stable at normal ambient conditions, and environmental corrosion under various conditions of temperature and humidity becomes a major issue. For this reason zinc electrodes are rarely used in DC capacitor applications, where electrochemical corrosion due to environmental conditions can be a dominant electrode failure mechanism. Zinc metallized films produced for AC capacitors are packaged in sealed bags with a desiccant, and precautions are taken not to wind the capacitor rolls in a high humidity environment.

Polymer Film Materials

Polymer films used as capacitor dielectrics are produced by manufacturing methods similar to those used in the production of common packaging films. Films such as polyester(PET) and polypropylene (PP) are extruded from a homogenized melt that is pressed through a flat-slot die. The condensed melt is stretched bi-axially for increased mechanical strength and it is thermally stabilized. Other polymer films like polycarbonate (PC) and PVDF are cast from a solution on a cooled drum and are dried before winding in a long oven. The surface of most films can be modified to suit a particular application. Surface roughness is attractive for general handling of films that includes slitting, winding, metallizing, etc. Some surface roughness is also advantageous in liquid impregnated capacitors. For metallized capacitor applications the surface of the film needs to be relatively smooth, to better control capacitance tolerance and to minimize the level of corona. Some minor surface roughness is acceptable and in most cases necessary for optimum winding conditions.

Capacitor films can be categorized into polymer films used for AC and DC applications. The most commonly used materials are PP for most AC applications, PET for most DC applications. PC, Polyphenilene sulfone (PPS) and polyethelene naphthalene (PEN)films are also used in used in some higher temperature AC and DC applications.

RELATIVE VOLUME OF METALLIZED CAPACITOR FILMS

Polypropylene: Highest Volume
- Used Mostly in Low Loss AC and High Rep-Rate Pulse Applications
- Typical thickness: 4µm to 12µm

Polyester: Moderate Volume
- Used Mostly in DC and low Rep-Rate Pulse Applications
- Typical Thickness: 1.2µm to 20µm

Other Films: Very low Volume
- Higher Temperature and Energy Storage Applications

METALLIZING EQUIPMENT EVOLUTION TO ACCOMMODATE NEW CAPACITOR ELECTRODES

Since the conversion from aluminun to Zn based electrodes, the poor nucleation properties of evaporated Zn in conjunction with its relatively poor atmospheric corrosion resistance, has forced the industry to explore various metallized electrode systems some of which are listed below:

Al/Zn Alloy—Thin Layer of Aluminum Deposited Prior to the Zn with some Mixing in the Interface

Ag + Zn—Silver is used to Nucleate the Zn Layer

Al + Zn—Two Layer

Cu + Zn—A thin Layer of Copper Oxide is used to Nucleate the Zn

Ag + Zn + Al

Al + Zn + Ag

Al + Zn + Al

Al + Ag + Zn + Ag

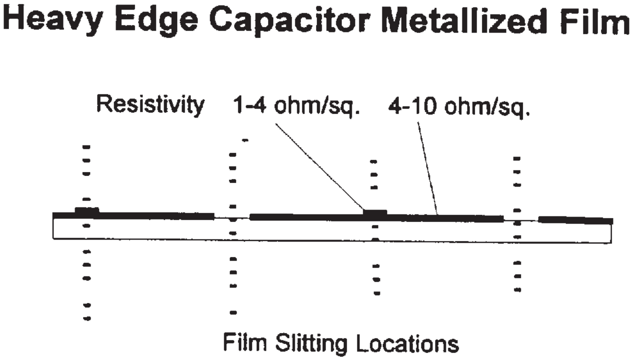

Figure 2. Additional metal is deposited in areas where the metallized electrode is contacted when the capacitor is formed.

Capacitor metallizing chambers have to employ multideposition sources in order to accommodate the different electrode systems. In order to maintain high process speeds, all the materials are evaporated using resistive heating. The evaporation is performed in the following manner.

Zn is Evaporated Using A Vacuum Furnace

Silver as a Nucleating Layer is Evaporated Using a Round Bar that is Heated with Current, with Pockets that Accept Ag Charges in the form of "Pills"

Al Is Evaporated Using:

1. Conventional Resistive Boats
2. A Single Long Boat Equal to the Film Width with Multiple Wire Feeds

Silver as a Thicker Coating is Also Evaporated from a Single Boat with Multiple Wire Feeds.

Other Unique Features of Capacitor Metallizing Machines

1. **Heavy Edge Electrodes:** As shown in Figure 2, additional thickness of metallization is required in areas that the metallized electrodes are contacted to carry capacitive current. This is accomplished by special masks in the Zn and/or aluminum deposition zones.

2. **Machine Direction Demetallized Zones:** This is usually accomplished with the use of masking bands that are arranged as shown in Figure 3.

3. **Segmented Electrodes:** Capacitor electrodes are segmented to improve the self healing process and reduce the probability of catastrophic failure by a thermal runaway mechanism. As shown in Figure 3, an oil printing system is used to print various patterns on the film prior to the metallization which prevents metal deposition. This technique can also be used to in place of the MD band masks. The demetallized lines can be made very fine, which is necessary to minimize electrode loss.

4. **Handling of Ultra Thin PET Films:** Capacitor metallizing machines have special web handling system to accommodate the metallization of very thin films. PET films with a thickness of 1.2µm are regularly metallized and some machines can handle PET films with thicknesses as low as 0.6µm.

5. **In-line Electrode Resistivity Measurement:** Capacitor machines in addition to optical density measuring equipment are also equipped with resistance measuring systems. These are usually based on direct conductivity measurement between two isolated rollers, or on Eddy current measuring sensors.

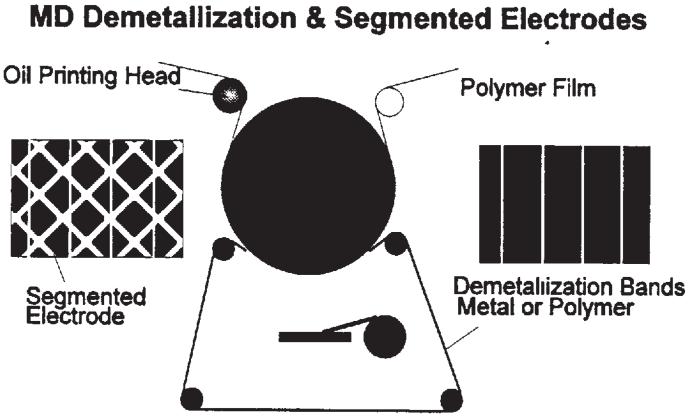

Figure 3. Schematic representation of a capacitor metallized film that is demetallized in specific areas using band masking and oil printing techniques.

CONCLUSIONS

- Metallized Capacitor Films Utilize the Same Basic Metallizing Technology as Packaging Metallizers

- Capacitor Film Metallization Requires Additional Refinements in Metallizing Technology
  - –Advance Tension Controls for Thin Films
  - –Techniques for In line MD and CMD Demetallization
  - –Additional Metal Evaporation Sources
  - –Often More than two Metallization Drums
  - –In line Measurement of Electrode Resistance

- The Performance of the Zn Based Electrodes is Just Adequate

- Future Growth May be Stimulated with the Advent of New Corrosion Stable Electrodes

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