POLITECNICO DI MILANO

School of Industrial and Information Engineering
Master Degree in Materials Engineering and Nanotechnology
Department of Chemistry, Materials and Chemical Engineering
"Giulio Natta"

IMPREGNATION TECHNIQUE ASSESSMENT ON THE ELECTROCHEMICAL BEHAVIOUR OF AN ALUMINIUM ELECTROLYTIC CAPACITOR

Supervisor: Prof.ssa	Paola GALLO STAMPINO
Co-supervisor: Ing.	Saverio LATORRATA
Co-supervisor: Ing.	Luca PRIMAVESI

Master thesis of:
Claudio Aguzzoli
Matricola: 878080

Academic Year 2017/2018

SUMMARY

INDEX OF FIGURES

INDEX OF TABLES

Riassunto

A causa dalla continua crescita della popolazione mondiale, il bisogno energetico è in continuo aumento anno dopo anno.

Le problematiche legate al consumo di energia sono sempre attuali e fonte di continui studi. In particolare per quanto riguarda la produzione e lo stoccaggio di energia, dalla scoperta della corrente elettrica fino ai nostri giorni, sono stati utilizzati diversi tipi di condensatori per immagazzinare nel modo più conveniente possibile l'energia elettrica.

Di grande interesse sono i condensatori elettrolitici in alluminio, in grado di accumulare energia grazie agli alti valori di capacità.

Il passo fondamentale che ha portato allo sviluppo dei primi condensatori elettrolitici è stato la scoperta di alcuni di metalli che si passivano naturalmente (per esempio alluminio o tantalio).

Questi metalli furono riconosciuti nel 1880 per la loro capacità di condurre la corrente elettrica in una sola direzione ed impedire il flusso di corrente nella direzione opposta grazie alla formazione di uno strato di ossido sulla superficie degli stessi, quando immersi in un elettrolita appropriato.

L'ossido si forma sulla superficie dell'anodo in seguito ad un processo elettrochimico, lo strato di ossido lavora come dielettrico, la soluzione elettrolita (che deve essere conduttiva), di cui è impregnata la carta separatrice, funge da connettore tra l'ossido dielettrico ed il catodo.

Dall'invenzione avvenuta nel 1880, all'invenzione del moderno condensatore elettrolitico ad alluminio nel 1925, vi è stato un continuo sviluppo sulla conoscenza alla base di questo tipo di condensatore e alla base del processo di funzionamento.

Con la crescita del industria elettrica, sono richiesti nuovi mezzi per lo stoccaggio di energia e i metodi vecchi vanno raffinati e ottimizzati: ne è un esempio lo studio e lo sviluppo del processo di incisione elettrochimico (etching) atto ad incrementare la superficie dell’anodo, in modo da aumentare l’area dell’interfaccia dielettrico - conduttore.

In questo elaborato viene analizzata la fase di impregnazione che è alla base del processo di produzione di un condensatore elettrolitico.

In particolare, vengono analizzati tutti i materiali forniti dall’azienda Itelcond, leader nel mercato italiano nel campo dei condensatori. Itelcond produce condensatori per applicazioni professionali ed industriali, caratterizzati da alti valori di capacità e applicabili per alti voltaggi.

Questi materiali principalmente sono le carte utilizzate come separatori, le soluzioni elettrolitiche ed i fogli di alluminio. Nello studio i materiali vengono caratterizzati prima e dopo il test, in modo da poter avere un quadro preciso su processo di impregnazione e sulla correlazione impregnazione - capacità.

Nei primi tre capitoli, dopo una panoramica generale sui condensatori, viene fornita una conoscenza di base sul processo di produzione di un condensatore elettrolitico ad alluminio ed i tipici parametri elettrici che lo caratterizzano.

Nel capitolo successivo viene riportata una lista dei materiali che formano un condensatore elettrolitico, seguita da una breve descrizione.

La spiegazione dettagliata del lavoro svolto in laboratorio, con una breve descrizione dei metodi utilizzati per caratterizzare questi campioni, è riportata nel capitolo quinto.

Successivamente è riportato il dettaglio delle prove di impregnazione effettuate con i risultati ottenuti.

Dall'analisi dei risultati ottenuti dai test di impregnazione è emerso che il tipo di carta separatrice utilizzata e la natura della soluzione elettrolitica influenzano l'efficacia del processo di impregnazione quanto la variazione di temperatura o di durata del processo.

Attraverso l'impregnazione di singoli provini di carta è possibile notare che il miglior risultato in termini di efficacia si ottiene immergendo i campioni nella soluzione più viscosa ed utilizzando i parametri standard del processo (cioè senza riduzioni di temperatura e di durata del processo).

Attraverso una analisi delle misure del peso è possibile calcolare la quantità in grammi su centimetro cubo del soluto intrappolato nel volume di carta, questo valore di impregnazione è confrontabile con gli altri valori ottenuti dalle altre prove svolte con parametri differenti.

Dalle misure ottenute, si riscontra che impregnando con soluzione elettrolita un condensatore già arrotolato, prima in condizioni standard e poi a temperatura ridotta, è presente una correlazione tra i provini analizzati.

Questa tendenza mostra che la differenza in peso del campione, dovuto al soluto impregnato nella carta, subisce un dimezzamento in peso nel caso di una riduzione di 20°C nella temperatura del processo.

Nel capitolo finale due condensatori ottenuti a seguito di processi di impregnazione effettuati con la medesima soluzione ma a temperature differenti (pari a 85°C e 65°C) vengono messi a confronto attraverso prove elettriche di carica, in modo da valutare le capacità dei condensatori.

Abstract

Since the world population keeps increasing, the energetic demand is constantly growing.

Issues related to the energy consumption are always topical, especially those regarding energy production and storage.

Since the discovery of electricity, different capacitors have been used in order to store energy in the most effective way.

In this field aluminium electrolytic capacitors are a good choice. They are capacitors able to store a lot of energy, due to their high capacitance values.

The turning point that led to the development of the first electrolytic capacitors was the discovery of certain valve metals, such as aluminium or tantalum.

These metals were considered in 1880, because of their ability of conducting charges in one direction only, while avoiding the flux of current the opposite direction, due to the oxide layer growing on their surface. The oxide forms on the surface of the anode after an electrochemical process, and it acts as a dielectric layer, while the electrolytic solution (that must be ionically conductive and must impregnate the paper separator), acts as a connector between the dielectric oxide and the cathode foil.

Thanks to the development of the electric industry, new methods for the energy storage are needed. An example is the development of the electrochemical etching process, that aims at increasing the surface of the anode, so that the interface between the dielectric oxide on the anode and the conductive plate will increase too.

More in detail, in this thesis the impregnation process, that is the basis of the production process of an aluminium electrolytic capacitor, has been analysed.

To do so, the materials supplied by Itelcond company have been used. Itelcond is an Italian industry that produces high voltage capacitors for professional use.

The materials supplied by the company are paper separators, electrolytic solutions and aluminium foils. These materials have been characterized before and after the impregnation test, with the purpose of having a precise overview on the impregnation process and the resulting electrical properties.

In the first chapters, after a general overview on the capacitors, a general explanation about the production process of the aluminium electrolytic capacitors and the typical related electrical parameters is given.

Then in the following chapters the materials and all the details and information about operating condition of the laboratory test are listed.

The last chapter reports result of the impregnation tests.

From the analysis of these results, it emerged that the kind of paper separators and the behaviour of the electrolytic solutions have an influence on the effectiveness of the impregnation process, as much as the temperature variation and the duration of the process.

Through the impregnation of each paper sample and the related characterization analyses it has been possible to understand that the most efficient method is to immerse the paper samples in the most viscous solution at standard conditions.

Afterwards the standard parameters of the process have been varied, decreasing the temperature and the duration of the process. This allowed to highlight that there is a difference in weight if the temperature is reduced by 20°C.

The next and last step of this thesis was the comparison between the trends resulting from impregnation of two electrolytic capacitors at 85°C and 65°C, and the charge test carried out on capacitors impregnated in the same conditions.

CHAPTER 1:

History and general characteristics about electrolytic capacitor

1.1 - Capacitors: a brief introduction

A capacitor is a passive two terminal electrical component that store potential energy in an electric field. The main effect of capacitors is known as capacitance, capacitance exists between any two electrical conductors in proximity in a circuit, a capacitor is a component designed to add capacitance to a circuit.

The physical form and construction of practical capacitors vary widely for this reason many capacitors types are in common use.

Most capacitors contain at least two electrical conductors often in the form of metallic plates of surfaces separated by a dielectric medium [1].

A conductor may be a foil, thin film, sintered bead of metal, or an electrolyte. The non-conductive dielectric acts in order to increase the capacitor's charge capacity.

Materials commonly used as dielectric include glass, ceramic, plastic film, paper, mica and oxide layers. Capacitors are widely used as parts of electrical circuits in many common electrical devices. Unlike a resistor, an ideal capacitor does not dissipate energy.

Capacitors store energy as well as charge.

These charges are stored on conductive plates, the positively charged plate is the anode and the negatively charged plate is the cathode [2].

In order to keep the charges separate, the medium between the anode and cathode, called the dielectric, must be non-conductive, an electrical insulator.

There are different types of dielectric materials on the market, list below the most used materials, with the relative dielectric constant [3].

Dielectric material / Relative dielectric constant "ε":

- Air or vacuum: 1.0
- Polypropylene: 2.2
- Polyester (Mylar): 3.0
- Mica: 6.0
- Aluminum oxide: 8.5
- Tantalum pentoxide: 27
- Niobium oxide: 41
- Barium titanate: 1000 - 10000

1.2 - Theory of operation

When two conductors experience a difference in potential, for example, when a capacitor is attached across a battery, an electrical field develops in the dielectric medium, causing a net positive charge to collect on one plate and net negative charge to collect on the other plate.

No current actually flows through the dielectric, however, there is a flow of charge through the source circuit. If the condition is maintained sufficiently long, the current through the circuit ceases. However, if a time varying voltage is applied across the leads of the capacitor, the source experiences an ongoing current due to the charging and discharging cycles of the capacitor [4].

From Coulomb's law a charge on one conductor will exert a force on the charge carriers within the other conductor, attracting opposite polarity charge and repelling as polarity charges, thus an opposite polarity charge will be induced on the surface of the other conductor. The conductors thus hold equal and opposite charges on their surfaces, and the dielectric develops an electric field.

An ideal capacitor is characterized by a constant capacitance C, defined as the ratio of the positive or negative charge "Q" on each conductor plate, to the voltage "V" between them:

$$C = \frac{Q}{\Delta V}$$

The capacitance's unit of measure in the international system of units (SI system of units) is the farad, defined as one coulomb per volt.

Typical capacitance values of capacitors for use in general electronics vary from about one p-farad to about one m-farad. A capacitance of one farad (F) means that one Coulomb of charge on each conductor causes a voltage of one volt across the device.

Because the conductors are close together, the opposite charges on the conductors attract one another due to their electric fields, allowing the capacitors to store more charge for a given voltage than when the conductors are separated, yielding a larger capacitance.

In practical device, charge build-up sometimes affects the capacitor mechanically, therefore the value of capacitance could vary.

In this case, capacitance is defined in terms of incremental changes: C=dQ/dV

It must be said that the capacitance of a capacitor is proportional to the surface area of the plates (conductors) and inversely related to the distance gap between them:

$$C = S\frac{\varepsilon}{d}$$

In practice, the dielectric between the plates passes a small amount of leakage current. It has an electric field strength limit, known as the breakdown voltage. The conductors and leads introduce an undesired inductance and resistance [5].

1.3 - General use of capacitors

Capacitors are widely used in electronic circuits for blocking direct current while allowing alternating current to pass. In analogic filter networks, they smooth the output of power supplies. In resonant circuits they tune radios to particular frequencies.

In electric power transmission systems, they stabilize voltage and power flow.

The property of energy storage in capacitors was exploited as dynamic memory in early digital computers [1] [6].

1.4 - History of capacitors

In 1745, Ewald Georg Von Kleist of Pomerania, Germany, found that charge could be stored by connecting a high-voltage electrostatic generator by a wire to a volume of water in a hand-held glass jar. Von Kleist’s hand and the water acted as conductor, and the jar as a dielectric (although details of the mechanism were incorrectly identified at the time).

The following year, the Dutch physicist Pieter van Musschenbroek invented a similar capacitor, which was named the Leyden Jar.

Leyden Jar Was the first capacitor and was invented in 1745 by Pieter van Musschenbroek, a physicist and mathematician in Leiden, Netherlands. It was a simple glass jar coated inside and outside with metal foil. Later, Leyden jars, were made by coating the inside and outside of jars with metal foil, leaving a space to prevent arcing between the foils.

The earliest unit of capacitance was the jar: equivalent to about 1.11 nanofarad.

Leyden jars or other more powerful devices employing flat glass plates alternating with foil conductors were used exclusively up until about 1900, when the invention of wireless (radio) created a demand for standard capacitors, and the steady move to higher frequencies required capacitors with lower inductance. More compact construction methods began to be used, such as a flexible dielectric sheet (like oiled paper) sandwiched between sheets of metal foil, rolled or folded into a small package [7].

Since the beginning of the study of electricity non-conductive materials like glass, porcelain, paper and mica have been used as insulators. These materials some decades later were also well suited for further use as the dielectric for the first capacitors. Paper capacitors made by sandwiching a strip of impregnated paper between strips of metal, and rolling the result into a cylinder were commonly used in the late 19th century.

Porcelain was used in the first ceramic capacitors, mica dielectric capacitors were invented in 1909 by William Dubilier. Prior to World War II, mica was the most common dielectric for capacitors in the United States [8] [9].

1.5 - History About electrolytic capacitors

Now let's analyse specifically about electrolytic capacitors. Their invention is around 1880, the invention of the modern Al electrolytic capacitor structure in 1925. In 1875, French researcher Eugene Ducretet discovered that certain "valve metals" (aluminium and others) can form an oxide layer that blocks an electric current from flowing in one direction but allows it to flow in the reverse direction [6].

Charles Pollak (born Karol Pollak), found out that the oxide layer on an aluminium anode remained stable in a neutral or alkaline electrolyte, even when the power was switched off. In 1896 he was granted U.S. Patent No. 672,913 for an "Electric liquid capacitor with aluminium electrodes". Pollak described his invention as a liquid condenser with aluminium electrodes, which are covered with a uniformly insulating layer generated by forming with a weak current, characterized by using an alkaline or neutral electrolyte. Since the insulating layer is very thin, the condenser has a very high capacitance and could be used as a polarized capacitor in a DC circuit [10].

Early electrolytic capacitors consisted of an aluminium electrode in a “bath” of electrolyte. In the first capacitor devices the resistance of the electrolyte resulted in a relatively high equivalent series resistance (ESR), and the capacitors were both bulky and heavy, although not relative to the alternatives at the time.

Mains-operated radio receivers, introduced around 1927, created a large consumer market for capacitors, which were required to produce ripple-free DC voltages.

The first electrolytic capacitors realized industrially consisted of a metallic box used as cathode, filled with a borax electrolyte dissolved in water, in which a folded aluminium anode plate was inserted. Applying a DC voltage from outside, an oxide layer was formed on the surface of the anode. The advantage of these capacitors was that they were significantly smaller and cheaper than all other capacitors at this time with respect to realized capacitance value. This construction with different styles of anode construction but with a case as cathode and a container as the electrolyte was used up to the 1930s and was called a "wet" electrolytic capacitor, referring to its high water content [11].

The first common application of wet aluminium electrolytic capacitors was in large telephone exchanges, to reduce relay hash (noise) on the 48 volt DC power supply [12].

The ancestor of the modern electrolytic capacitor was patented by Samuel Ruben in 1925. He introduced a separate second foil to contact the electrolyte adjacent the anode foil instead of using the electrolyte-filled container as the cathode of the capacitor. The stacked second foil got its own terminal additional to the anode terminal and the container had no longer an electrical function. This type of electrolytic capacitor with one anode foil separated from a cathode foil by a liquid or gel-like electrolyte of a non-aqueous nature, which is therefore dry in the sense of having a very low water content, became known as the "dry" type of electrolytic capacitor. This invention, together with the invention of wound foils separated with a paper spacer in 1927 by A. Eckel, Hydra-Werke in Germany, reduced the size and the price significantly, and these helped make the new radios affordable for a broader group of customers [11].

The old wax capacitors (before 1900) are limited to 1 or 2 μF, so they had to be combined with bulky chokes (inductors) to produce efficient power frequency filters. Instead electrolytic capacitors provided much greater capacitance so that the chokes were not necessary, although early electrolytic capacitors used in radio receivers still consisted of an oxidized anode in a bath of electrolyte [9].

The period after World War II is associated with a rapid development in radio and television technology as well as in industrial applications, which had great influence on production quantities but also on styles, sizes and series diversification of electrolytic capacitors. New electrolytes based on organic liquids reduced leakage currents and ESR, broadened temperature ranges and increased lifetimes. Corrosion phenomena caused by chlorine and water could be avoided by a higher purity manufacturing processes and by using additives in the electrolytes.

The development of tantalum electrolytic capacitors in the early 1950s with manganese dioxide as solid electrolyte, which has a 10 times better conductivity than all other types of non-solid electrolytes, also influenced the development of aluminium electrolytic capacitors. In 1964 the first aluminium electrolytic capacitors with solid electrolyte (solid aluminium capacitor: SAL) appeared on the market, developed by Philips.

The decades from 1970 to 1990 were marked by the development of various new professional aluminium electrolytic capacitor series with specific peculiarities, for example capacitors with very low leakage currents or with long life characteristics or for higher temperatures up to 125°C. These capacitors were specifically suited to certain industrial applications, the great diversity of the many series of aluminium electrolytic capacitors with non-solid electrolytes up to now is an indicator of the adaptability of the capacitors to meet different industrial requirements [11].

CHAPTER 2:

Classification and improvement methods in aluminium electrolytic capacitor

2.1 - Electrolytic capacitors

Electrolytic capacitors are capacitors in which one or both of the "plates" is a non-metallic conductive substance, an electrolyte. Electrolytes have lower conductivity than metals, so these electrolytes are used only in capacitors when metallic plate is not practical, such as when the dielectric surface is fragile or rough in shape or when ionic current is required to maintain the dielectric integrity. The dielectric material of electrolytic capacitors is formed from the anode metal itself in what is known as the forming process or anodizing process. During this process, current flows from the anode metal through a conductive bath of a special forming electrolyte to the bath cathode [3] [13].

The anode material must be a valve metal such as aluminium, niobium, tantalum, titanium because the flow of current causes an insulating metal oxide to grow on the surface of the anode. The thickness, structure and composition of this insulating layer determine its dielectric strength. The applied potential between the anode metal and the bath cathode must be above the oxide breakdown voltage before significant current will flow. As current flows, the breakdown strength (formed voltage) and oxide thickness increase.

A relationship between the charge flow through the system and the amount of product (in this case, metallic oxide) was found to exist by Faraday, he noted the relationship between gram-equivalents of product and charge transfer for all ideal (stoichiometric) electrolysis reactions in what is known as Faraday's Law.

In the formation process, brittle metallic oxide is grown upon the metal foil, which is usually rough in shape. The anode metal is therefore in intimate contact with one side of the oxide dielectric. The electrolyte is used to make contact between the other side of the oxide formed on anode and the cathode plate [6].

Due to their very thin dielectric oxide layer and enlarged anode surface, electrolytic capacitors have a much higher capacitance-voltage product per unit volume compared to ceramic capacitors or film capacitors, and so can have large capacitance values.

The advantage of electrolytic capacitors is the high capacitance per unit volume and per unit cost. The high capacitance arises from the high dielectric constant, the high breakdown field strength, the rough surface, and the extremely small, uniform thickness of the anodic formed metallic oxide.

The reason that electrolytic capacitors have such uniform dielectric stress and can operate at such high field strength, within 80% of their breakdown strength, on the order of 1000 volts/µm, is due to two reasons:

- The original anodization process is performed at a fixed voltage, and the dielectric grows everywhere to whatever thickness is required to support that voltage.
- Once the foil is in a capacitor, the capacitor "fill" electrolyte continues the healing work of the original forming electrolyte, repairing and thickening the dielectric locally as required.

This healing process is driven by the capacitor's DC leakage current, which is drawn whenever a DC voltage is applied to the capacitor, that is, whenever it is in operation. For these reasons, electrolytic capacitors often last longer when they are in a continuous, mild use than when they are charged up briefly only every year or more time.

The large capacitance of electrolytic capacitors makes them particularly suitable for many different applications, like as passing or bypassing low-frequency signals or for storing large amounts of energy.

The disadvantage of electrolytic capacitors is: the non-ideal loss of characteristics, which arise from the semi-conductive oxide properties, double-layer effects from the electrolyte-oxide charge-space region, resistive losses from the high electrolyte resistivity, frequency response roll-off due to the roughness of the surface oxide, and finite capacitor life due to breakdown and degradation of the electrolyte.

Electrolytic capacitors are considered as polarized components due to their asymmetrical construction, and must be operated with a higher voltage (more positive) on the anode than on the cathode at all times. For these reasons the anode terminal is marked with a plus sign and the cathode with a minus sign. Applying a reverse polarity voltage or a voltage exceeding the maximum rated working voltage of as little as 1 or 1.5 volts, can destroy the dielectric and thus the capacitor. The failure of electrolytic capacitors often can be hazardous, resulting in an explosion or fire. Bipolar electrolytic capacitors which may be operated with either polarity also exist, this is possible by using special constructions with two anodes connected in series [14].

2.2 - Electrolytic capacitors family tree

Depending on the type of valve metal used as a conductor, it possible find three different big families of electrolytic capacitor:

- Aluminium electrolytic capacitors

- Tantalum electrolytic capacitors
- Niobium electrolytic capacitors

As to the basic construction principles of electrolytic capacitors, there are three different types: aluminium, tantalum, and niobium capacitors.

Each of these three capacitor families uses non-solid and solid manganese dioxide or solid polymer electrolytes, so a great spread of different combinations of anode material and solid or non-solid electrolytes is available [15].

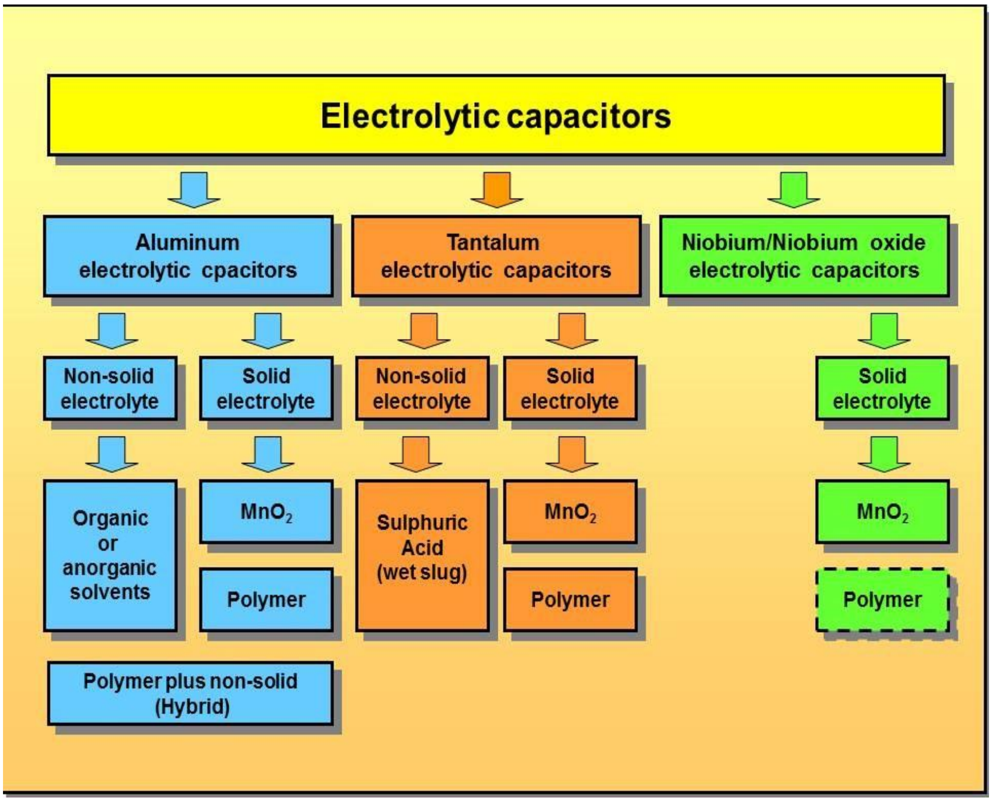

Fig. n°1: Family three of electrolytic capacitor

2.3 - Aluminium electrolytic capacitors

Considering the vastness of the possible combination of electrolytic capacitors, the focus of this thesis is on the type of electrolytic aluminium capacitor with non-solid electrolyte, in order to the fact that it is the type that will be analysed in detail in the laboratory.

An aluminium electrolytic capacitor consists of anode and cathode aluminium foil, capacitor paper (electrolytic paper), electrolyte, and an aluminium oxide film, which acts as the dielectric, formed on the anode foil surface.

Aluminium electrolytic capacitors are polarized electrolytic capacitors whose anode, the positive electrode, is made of a pure aluminium foil with an etched surface. The aluminium forms a very thin insulating layer of aluminium oxide by anodization that acts as the dielectric of the capacitor. This very thin oxide film formed by electrolytic oxidation (formation) offers superior dielectric constant and has rectifying properties [16].

A non-solid electrolyte covers the rough surface of the oxide layer, serving in principle as the second negative electrode, the cathode of the capacitor. A second aluminium foil called “cathode foil” contacts the electrolyte and serves as the electrical connection to the negative terminal of the capacitor.

When in contact with an electrolyte, the oxide film possesses an excellent forward direction insulation property.

Together with improved effective surface area attained by etching the foil, higher capacitance allowed a substantial reduction in size of the capacitor.

As previously mentioned, an aluminium electrolytic capacitor is constructed by using two strips of aluminium foil (anode and cathode) with paper interleaved.

Both the foils and paper are then wound into an element and impregnated with electrolyte.

Since the oxide film has rectifying properties, a capacitor has polarity. If both the anode and cathode foils have an oxide film, the capacitors would be bipolar (non-polar) type capacitor. These technical notes refer to "non-solid" aluminium electrolytic construction in which the electrolytic paper is impregnated with liquid electrolyte. There is another type of aluminium electrolytic capacitor, which is the "solid" that uses solid electrolyte [6].

Aluminium electrolytic capacitors are divided into three subfamilies by the type of electrolyte:

- Non-solid (liquid, wet) aluminium electrolytic capacitors
- Solid manganese dioxide aluminium electrolytic capacitors
- Solid polymer aluminium electrolytic capacitors

Aluminium electrolytic capacitors with non-solid electrolyte are the most inexpensive type and also are those with widest range of sizes, capacitance and voltage values.

They are characterized by capacitance values from 0.1 µF up to 2,700,000 µF (2.7 F) and rated voltages values from 4 V up to 630 V.

The liquid electrolyte provides oxygen for re-forming or self-healing of the dielectric oxide layer. However, it can evaporate through a temperature-dependent drying-out process, which causes electrical parameters to drift, limiting the service lifetime of the capacitors.

Different types of aluminium electrolytic capacitors exist.

An overview of the different types of aluminium electrolytic capacitors in order to highlight the differences is given.

Aluminium electrolytic capacitors are divided into two sub-types depending on whether they make use of liquid or solid electrolyte systems. Because the different electrolyte systems can be constructed with a variety of different materials, they include further sub-types.

Aluminium electrolytic capacitors with non-solid electrolyte use a liquid electrolyte of that type:

- Based on ethylene glycol and boric acid, so-called “borax” electrolytes.
- Based on organic solvents, such as DMF, DMA, GBL.
- Based on high water containing solvents, for so-called "low impedance", "low ESR" or "high ripple current" capacitors.

Due to their relatively high capacitance values aluminium electrolytic capacitors have low impedance values even at lower frequencies like mains frequency.

They are typically used in power supplies, switched-mode power supplies and DC-DC converters for smoothing and buffering rectified DC voltages in many electronic devices as well as in industrial power supplies and frequency converters as DC link, capacitors for drives, inverters for photovoltaic, and converters in wind power plants. Special types are used for energy storage, for example in photoflash or strobe applications or for frequency coupling in audio applications [15].

2.4 - Construction details of aluminium electrolytic capacitor

An aluminium electrolytic capacitor with a non-solid electrolyte always consists of two aluminium foils separated mechanically by a spacer, mostly paper, which is saturated with a liquid or gel-like electrolyte. One of the aluminium foils, the anode, is etched (roughened) to increase the surface and oxidized (formed). The second aluminium foil, called the "cathode foil", serves to make electrical contact with the electrolyte. A paper spacer mechanically separates the foils to avoid direct metallic contact. Both foils and the spacer are wound and the winding is impregnated with liquid electrolyte. The electrolyte, which serves as cathode of the capacitor, has to cover perfectly the etched rough structure of the oxide layer on the anode surface. A good wetting process makes the increased anode surface effectual in order to increase capacitance of device. After impregnation the impregnated winding is mounted in an aluminium case and sealed [17].

The production process starts with mother rolls. First, the etched, roughened and pre-formed anode foil on the mother roll, the spacer paper and the cathode foil are cut to the required width. The foils are then inserted to an automatic winder, which makes a wound section in a consecutive operation involving three sequential steps: terminal welding, winding, and length cutting. To keep the wrapped shape, it is bound with tape.

In the next production step the wound section fixed at the lead out terminals is soaked with electrolyte under vacuum impregnation. The impregnated winding is then built into an aluminium case, provided with a rubber sealing disc, and mechanically tightly sealed by curling. Thereafter, the capacitor is provided with an insulating shrink sleeve film. This optically ready capacitor is then contacted at rated voltage in a high temperature post-forming device for healing all the dielectric defects resulting from the cutting and winding procedure [16].

2.5 - Production process

Metal tabs are attached to the anode and cathode plates, and the assembly is wound into a cylindrical section. The tabs are welded to aluminium terminals installed in a header (top). The section-header assembly is immersed in a bath of hot capacitor electrolyte.

In what is called the impregnation process, a vacuum is applied to the electrolyte to the wound sections immersed, causing electrolyte to be drawn into the sections, thoroughly wetting the sections. The sections are placed in aluminium cans, and the headers are sealed to the cans.

The capacitor units are slowly brought up to maximum rated voltage at maximum rated temperature during the aging process. The aging process grows oxide on areas on the anode foil which have an insufficient oxide barrier, such as slit edges and places which have been cracked during the winding operation. Inspections and tests occur at several stages of the production process. After post-forming, a final measurement of capacitance, leakage current, and impedance takes place [18] [19].

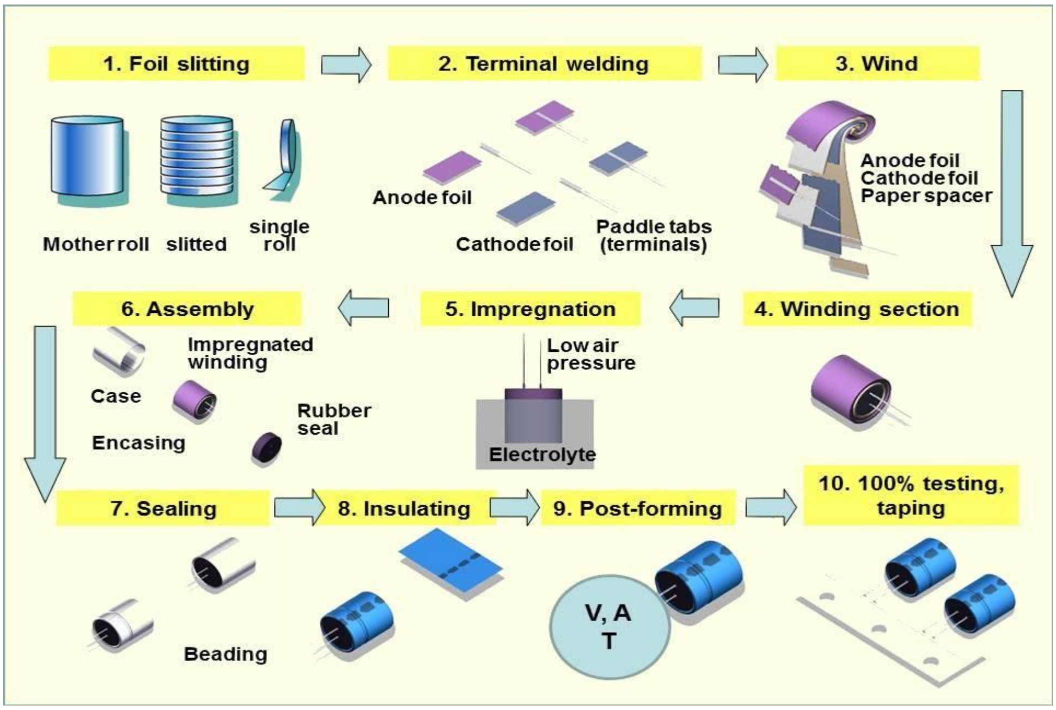

Fig. n° 2: Production process of aluminium electrolytic capacitor

By design, a non-solid aluminium electrolytic capacitor has a second aluminium foil, the cathode foil, for contacting the electrolyte. This structure of an aluminium electrolytic capacitor results in a characteristic result because the second aluminium (cathode) foil is covered with an insulating oxide layer naturally formed by air. Therefore, the construction of the electrolytic capacitor consists of two single series-connected capacitors with capacitance of the anode and capacitance of the cathode [6].

2.6 - Capacitance and Discharging Stability

The ingenious idea to introduce a second aluminium foil to contact the electrolyte, the so-called “cathode” foil, introduces a second capacitor in series with the primary dielectric on the anode as a result of the inevitable 1.5-V withstand oxide layer on the cathode formed by exposure to air. Therefore, the construction of an electrolytic capacitor consists of two series-connected capacitors with a capacitance CA of the anode and a capacitance CC of the cathode.

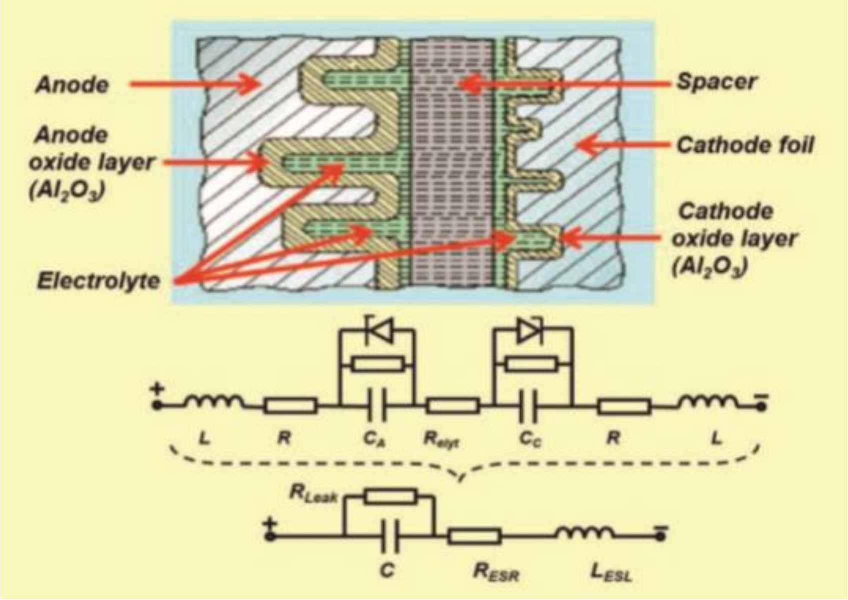

Fig. n°3: Two-series connected capacitors

The total capacitance of the non-solid aluminium electrolytic capacitor is thus obtained from the formula for the capacitance of two, series-connected capacitors:

$$C_{\text{e-cap}} = \frac{C_{\text{A}} \cdot C_{\text{C}}}{C_{\text{A}} + C_{\text{C}}}$$

The total capacitance, Ce-cap, is determined mainly by the anode capacitance CA when the cathode capacitance (CC) is at least 10 times greater than the anode capacitance (CA). Normally, this condition is achieved easily, as the capacitance per unit area of the very thin natural oxide layer on the slightly etched cathode foil is very large. A capacitor in an electrical circuit is expected to withstand all conditions that occur during normal operation. Power supply filters are the most common application of aluminium electrolytic capacitors, in which they must withstand near instantaneous application of rated voltage in low-impedance circuits without current limiting. The peak inrush current is limited by the ion mobility-induced ESR of the capacitor, so that every nonsolid Al e-cap is protected naturally from damaging inrush currents within its I^2R electro-thermal limits and cannot be damaged by large dI/dt, which can be damaging to the end connections of metallized film capacitors. During discharging, the current direction in the capacitor reverses, and the cathode becomes the anode. This results in an internal voltage distribution with reverse polarity on the anode and cathode foils, the magnitudes of which depend on the construction of the foils. If the reverse voltage on the cathode foil exceeds its naturally formed 1.5 V withstand, anodic oxidation takes place with the formation of a thicker oxide layer on cathode, which reduces the capacitor capacitance.

Most practical electrolytic capacitors with natural air-based 1.5 V withstand cathode oxide layers and a specific capacitance ratio between the cathode and anode oxides of at least 10 to 1, can sustain their naturally ESR-limited discharge current without exceeding 1.5 V on the cathode oxide during discharge and are therefore termed “discharge proof.” The capacitance ratio is typically greater than 10:1, and for applications with frequent charge-discharge cycles or for high-voltage e-caps, a ratio greater than 100:1 may be required for discharge-proof operation.

In all cases, this will be sufficient to prevent the cathode from anodizing during discharge. That also applies to applications with very high discharge currents, such as for photo-flash devices or defibrillators. Photo-flash electrolytic capacitors are often made with double anode technology to increase capacitance and thus the flash energy. Electrolytic capacitors with double-anode technology have two superimposed anode foils that are wound together with one cathode foil [6].

2.7 - Increasing Anode Surface: Capacitor Miniaturization

Soon after the introduction of wound foils for Al electrolytic capacitors, concepts emerged for increasing the specific capacitance of the anode. Initially, this was achieved through mechanical roughening of the anode surface prior to forming.

The use of electro-chemical etching from the mid-1930s onward increased the effective surface of the aluminium anode greatly.

During such etching, the foil runs through sequentially arranged electro-chemical etching baths in the presence of several thousand amps from the foil to the bath.

After cleaning, the roughened anode foil is oxidized and then cleaned again [20].

The pores etched into the aluminium surface has to be sufficiently large to accommodate the required oxide thickness and leave sufficient space for the electrolyte in the pore to provide adequate wetting and consequently conduction.

It is possible to arrange the electrolyte in order to make it fit better with the proper aluminium etched surface.

The etching conditions must be adjusted to obtain properties appropriate for the intended operating voltage.

For low-voltage electrolytic capacitors (6.3 to 100 V), sponge-like structures provided very large specific capacitance, whereas for high-voltage capacitors (160 to 630 V), tubular structures are typical to accommodate the greater oxide thickness while leaving space for the electrolyte to penetrate inside them.

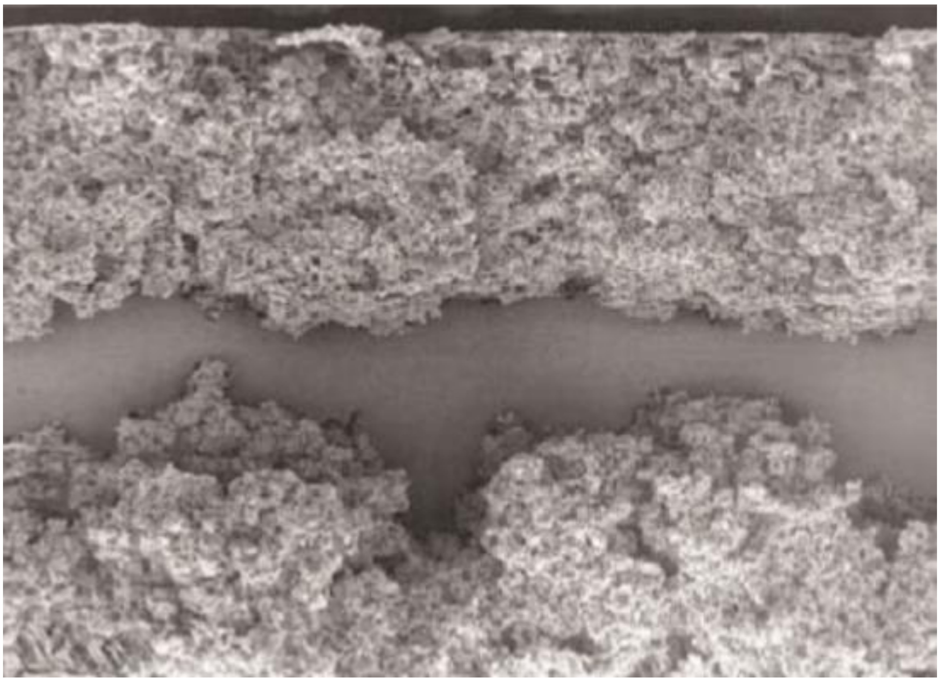

Fig. n°4: Sponge-like structure of etching performed for a low-voltage Al e-cap

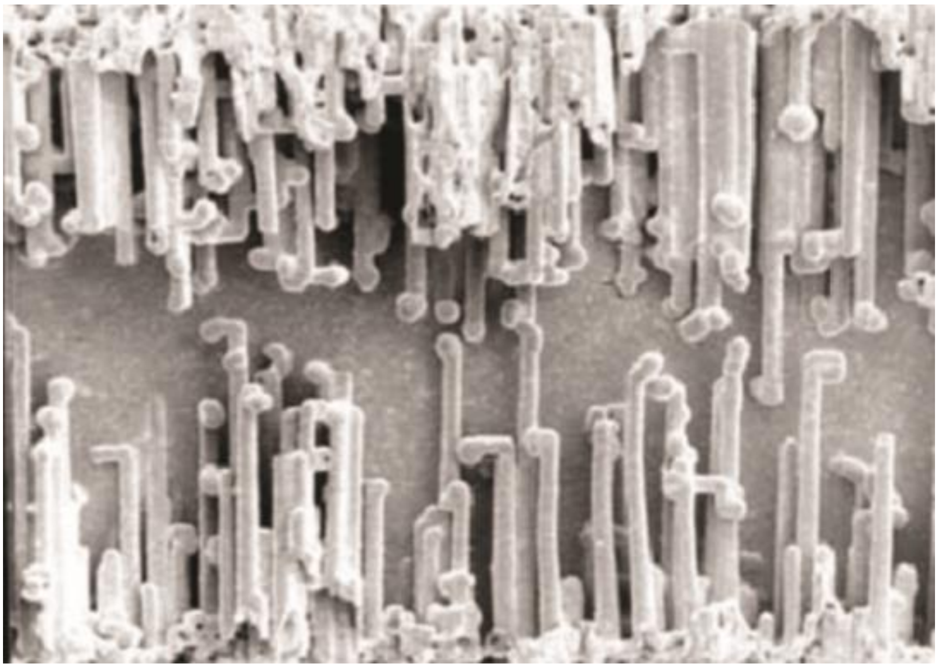

Fig. n°5: Tubular structure of etching for a high-voltage Al e-cap

The mechanical etching processes of the early 1930s could increase specific capacitance relative to a “flat” foil by about 30 times for low-voltage capacitors, by 2 to 4 times for high-voltage capacitors.

The present chemical etching processes can enhance low voltage specific capacitance by about 200 and the high voltage by about 30 times [3].

The increased specific capacitance of anode foils had reduced capacitors dimensions by roughly a factor of 10 over the last 50 years in electrolytic capacitor. However, with smaller pores, the ions in the electrolyte have to pass through smaller current paths, which increases the resistance so that more highly structured anodes (greater specific capacitance) cause increased ESR.

For these reasons, increased specific capacitance to reduce capacitor size have to be accompanied by improved electrolyte conductivity in order to maintain constant ESR, which determines the sustainable ripple current in filter applications [21].

2.8 - Uses and applications of aluminium electrolytic capacitors

Until about the mid-1950s, the largest markets for electrolytic capacitors were radio receivers and later television sets, as well as telephone systems, as filter capacitors for interference suppression. To a lesser degree, bipolar e-caps, made from two anode foils connected in opposite polarity, were used for coupling audio signals, in loudspeaker crossovers, and so on. “Motor start” capacitors for single-phase AC motors are another major market for e-caps. These latter two markets are still very active. Some years after the invention of the transistor, electronic technology started an ever more rapid evolution that continues today and has created many new markets for e-caps. New electronic technology facilitated improved electronic telephone systems, telegraph and facsimile equipment, electronic typewriters and printers, and so on, all of which required many electronic components. The electronic blinker was one of the first applications in the automobile industry. In the 1960s an automobile electronic blinker was constructed with discrete components that included a low-leakage-current electrolytic capacitor with very tight tolerance in series with a resistor to deliver the time constant for the blinker frequency. Also, the first ABS and safety belt controls in the late 1960s contained aluminium electrolytic capacitors [22].

The market for electronic equipment developed rapidly. We mentioned the use of e-caps in radio and television sets, and automotive blinker circuits, but also tape recorders, recording mixers, electric typewriters, cash machines, desktop computers, measuring instruments, speed controls for vacuum cleaners and drilling machines, radio remote controls, X-ray equipment, industrial machine controls, and heating controls. With the variety of new applications, the demand for high-quality components increased and was achieved as a result of improved material purity.

The most important applications include filter capacitors for power supply outputs, blocking and DC-bypass circuits, motor start and other non polarized capacitors, audio applications, energy discharge capacitors, photoflash and strobe capacitors.

The wide range of applications for capacitors creates many situations in which the design engineer must decide among differing capacitor technologies based on technical requirements. In the competition among capacitor technologies, overlaps occur that provide ever changing opportunities based on new developments.

Total worldwide usage of capacitors is approximately one trillion units per year. The total market value is approximately 17 billion dollars per year [6].

CHAPTER 3:

Typical electrical parameters of aluminium electrolytic capacitor

3.1 - Electrical parameters

Capacitors are components that are widely used in electrical circuits, for this reason this chapter is devoted to explain the most important electrical parameters used to characterize and classify a capacitor.

The electrical characteristics of electrolytic capacitors are concerted by the international generic specification IEC 60384-1.

In this standard, the electrical characteristics of capacitors are described by an idealized series-equivalent circuit with electrical components which model all ohmic losses, capacitive and inductive parameters of an electrolytic capacitor [23].

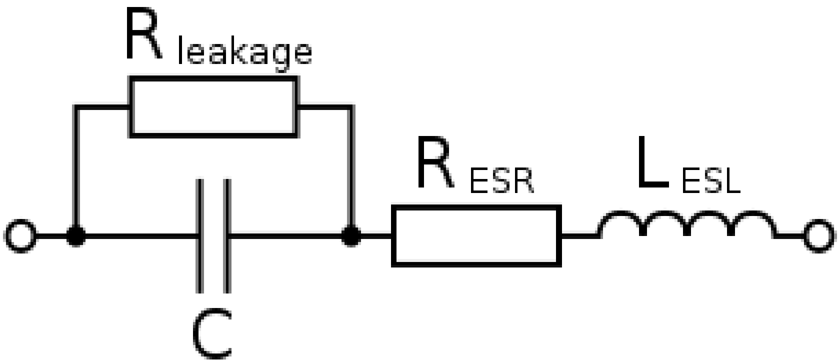

Fig. n°6: Series-equivalent circuit representation

3.2 - Capacitance, standard values and tolerances

The electrical characteristics of electrolytic capacitors depend on the structure of the anode and the electrolyte used.

This influences the capacitance value of electrolytic capacitors, which depends on measuring frequency and temperature during electrical measurement.

Electrolytic capacitors with non-solid electrolytes show a broader aberration over frequency and temperature ranges than in case of capacitors with solid electrolytes.

The basic unit of an electrolytic capacitor's capacitance is the microfarad (μF). The capacitance value specified in the table of data sheets of the manufacturers is called the rated capacitance or nominal capacitance and is the value for which the capacitor has been designed.

The standard for measuring condition for aluminium electrolytic capacitors is an AC measuring method with 0.5 V fixed at a frequency of 100-120 Hz and a temperature of 20°C.

The capacitance value measured at the frequency of 1 kHz is about 10% less than the 100-120 Hz value specified. Therefore the capacitance values of electrolytic capacitors are not directly comparable and differ from those of other type capacitors as film capacitors or ceramic capacitors, whose capacitance is measured at 1 kHz or higher.

Instead, measured with an AC measuring method with 100-120 Hz the capacitance value is the closest value to the electrical charge stored in the e-caps. The stored charge is measured with a discharge method and is called the DC capacitance. The DC capacitance is about 10% higher than the 100-120 Hz AC capacitance [14].

The DC capacitance is of interest for discharge applications (like photoflash).

The capacitance tolerance is the percentage of allowed deviation of the measured capacitance from the rated value.

Electrolytic capacitors are available in different tolerance series. Anyway the required capacitance tolerance is determined by the particular application. Electrolytic capacitors, often used for filtering and by-passing, do not need narrow tolerances because they are mostly not used for accurate frequency applications such as in oscillators [6].

3.3 - Rated and category voltage

The allowed operating voltage of a capacitor is called the "rated voltage".

The rated voltage is the maximum DC voltage or peak pulse voltage that may be applied continuously at any temperature within the rated temperature range.

The voltage proof of electrolytic capacitors, which is directly proportional to the dielectric layer thickness, decreases with increasing temperature.

For some applications it is important to use a high temperature range, lowering the voltage applied at a higher temperature maintains safety margins. For some capacitor types, therefore, the standard specifies a second "temperature de-rated voltage" for a higher temperature range, the "category voltage".

The category voltage is the maximum DC voltage, peak pulse voltage or superimposed AC voltage that may be applied continuously to a capacitor at any temperature within the category temperature range.

Applying a higher voltage than specified may destroy electrolytic capacitors.

Applying a lower voltage may have a positive influence on electrolytic capacitors.

For aluminium electrolytic capacitors a lower applied voltage may in some cases extend the lifetime [14].

3.4 - Reverse voltage

Standard electrolytic capacitors, aluminium as well as tantalum and niobium electrolytic capacitors, are polarized and generally require the anode electrode voltage to be positive relative to the cathode voltage.

Nevertheless, electrolytic capacitors can withstand for short instants a reverse voltage for a limited number of cycles. In detail, aluminium electrolytic capacitors with non-solid electrolyte can withstand a reverse voltage of about 1 V to 1.5 V.

It must be said that this reverse voltage should never be used to determine the maximum reverse voltage under which a capacitor can be used permanently, but in no case may a reverse voltage be used for a permanent AC application.

To minimize the possibilities that a polarized electrolytic being incorrectly inserted into a circuit, polarity has to be clearly indicated on the external case.

Special bipolar aluminium electrolytic capacitors designed for bipolar operation are available, and usually referred to as "non-polarized" or "bipolar" types. These capacitors have two anode foils with full-thickness oxide layers connected in reverse polarity, but these bipolar electrolytic capacitors are not adaptable for main AC applications [14].

3.5 - Impedance

Capacitors could be seen as a storage component for electric energy, but this is only one of the function of a capacitor.

A capacitor may also act as an AC resistor. Especially aluminium electrolytic capacitors in many applications are used as decoupling capacitors to filter or bypass undesired biased AC frequencies to the ground or for capacitive coupling of audio AC signals. Then the dielectric is used only for blocking DC. For these reasons, for such applications the AC resistance (the impedance), is as important as the capacitance value.

The impedance is a frequency-dependent AC resistance and possesses both magnitude and phase at a particular frequency.

The impedance *Z* is the vector sum of reactance and resistance, it describes the phase difference and the ratio of amplitudes between sinusoidal varying voltage and sinusoidal varying current at a given frequency.

In this way impedance is a measure of the ability of the capacitor to pass alternating currents and can be used like Ohm's law [23] [24].

3.6 - ESR and dissipation factor

The equivalent series resistance (ESR) summarizes all resistive losses of the capacitor.

These are the terminal resistances, the contact resistance of the electrode contact, the line resistance of the electrodes, the electrolyte resistance, and the dielectric losses in the dielectric oxide layer.

For electrolytic capacitors generally the ESR decreases with increasing frequency and temperature.

ESR influences the remaining superimposed AC ripple behind smoothing and may influence the circuit functionality. Related to the capacitor, ESR accounts for internal heat generation if a ripple current flows over the capacitor.

This internal heat reduces the lifetime of non-solid aluminium electrolytic capacitors [25].

3.7 - Leakage current

For electrolytic capacitors, DC leakage current is a special characteristic that other conventional capacitors do not have. This current is represented by the resistor $R_{(leak)}$ in parallel with the capacitor in the series-equivalent circuit of electrolytic capacitors.

The reasons for leakage current are different between electrolytic capacitors with non-solid and with solid electrolyte, for non-solid aluminium electrolytic capacitors, the leakage current includes all weakened imperfections of the dielectric caused by unwanted chemical processes, taking place during the time without applied voltage (storage time) between operating cycles.

These unwanted chemical processes depend on the kind of electrolyte, electrolytes with water content or water based electrolytes are more aggressive to the aluminium oxide layer than other electrolytes based on organic liquids are. This is why different electrolytic capacitor series specify different storage time without reforming instructions [26].

Applying a positive voltage to a "wet" capacitor causes a reforming (self-healing) process which repairs all weakened dielectric layers, and the leakage current remain at a low level. Although the leakage current of non-solid e-caps is higher than current flow over insulation resistance in ceramic or film capacitors, the self-discharge of modern non-solid electrolytic capacitors with organic electrolytes takes several times.

The specification of the leakage current is often given by multiplication of the rated capacitance value with the value of the rated voltage together with an addendum figure, measured after a measuring time of two or five minutes.

The leakage current value depends on the voltage applied, on the temperature of the capacitor, and on measuring time [27].

CHAPTER 4:

Aluminium Electrolytic Capacitor Materials

4.1 - List of the main components of an aluminium electrolytic capacitor

The principal components of an electrolytic capacitor made of aluminium are the following materials:

- Anode foil
- Anode oxide layer (dielectric)
- Cathode foil
- Cathode oxide layer
- Non-solid electrolyte
- Paper spacer soaked with electrolyte, either non-solid or polymer

Aluminium electrolytic capacitors with non-solid electrolyte are the best known and most widely used electrolytic capacitors, therefore these components can be found on almost all boards of electronic equipment.

These materials are characterized by particularly inexpensive and easy to process base materials [3] [18].

Aluminium capacitors with liquid electrolytes based on borax or organic solvents have a large range of types and ratings, but in general they can be summarized as follows.

A general description of the materials is given in the following sections.

4.2- Anode Foil

The anode foil can be made of various purities of aluminium, but for high voltage or high energy density electrolytic capacitors, the anode is generally comprised of at least 99.98% purity, high cubicity aluminium foil of about 100 micrometer thickness.

The term “high cubicity” refers to the rectangularly oriented aluminium grain structure which is intentionally produced in the foil [3].

The first production process this foil undergoes, as we have already said, is called etching, which electrochemically roughens the surface of the foil, causing hollow tunnels to grow into the aluminium.

The rectangular aluminium grain orientation causes the etched tunnels to form along parallel paths which are mostly perpendicular to the aluminium top surface. The etching process greatly increases the microscopic to macroscopic surface area ratio, which can be up to sixty for high-voltage aluminium electrolytic anode foil, and even higher for low-voltage foil. The foil emerges from the etching process considerably lighter in weight than it entered. The next process the roll of foil undergoes is called the formation process. Aluminium oxide is grown onto and into the hollow tunnels which were etched into the aluminium during the etching process. Notice that the inside diameter of this 550 volt oxide tunnel is about a quarter of a micrometer and that the wall thickness is a little more than one-half micro-meter. In general, the ratio of the oxide thickness to the oxide formation voltage is about 1.0 nano-meter per volt. This ratio varies somewhat with the oxide structure. Depending on formation, electrolyte composition, the current density, and other production parameters, the structure of the aluminium oxide may be amorphous, crystalline, hydrous, or some combination of these structures [6] [13].

Departures from this relationship exist for the process of oxide formation on anode metals, since some oxide can be grown chemically and thermally, it is possible to reduce the electrical energy requirements in the formation process, which can cost several dollars per kilogram of anode produced.

Also there can be some undesirable side reactions during the formation process which do not contribute to oxide formation [28].

4.3 - Cathode Foil

The cathode foil is made by different purities of aluminium, but in general less pure than anode.

The cathode aluminium foil is generally thinner than the anode and must exhibit much higher capacitance than the anode, since the cathode capacitance appears in series with the anode capacitance to yield the total capacitance.

For a given anode capacitance, the maximum total capacitance occurs when the cathode capacitance is as large as possible. High cathode capacitance requires a very low cathode formation voltage. Generally the cathode is not formed at all, but there is always a thin layer (around 2-3 nm) of hydrous oxide on the surface of aluminium unless it is passivated and the electrical double layer has a large capacitance. A thin hydrous oxide layer tends to form readily on aluminium surface with normal exposure to air in the atmosphere [13].

Such a high cathode capacitance is necessary only for low-voltage capacitors with high-gain anodes. Generally a cathode capacitance of fifty times the anode capacitance is sufficient. This situation yields a total capacitance which is only 2% less than the anode capacitance.

For a discharge capacitor, the charge on the anode plate must be neutralized by the opposite charge on the cathode plate, which requires that the cathode be capable of storing a charge greater than or equal to the anode charge.

In other words, the product of the capacitance and forming voltage must be larger for the cathode than for the anode. This requirement is generally achieved automatically, since the charge storage capability of formed foil is maximized at low formation voltage.

A thin foil is used for the cathode, giving a frequency response generally better than that of the anode, and giving a large enough capacitance so that the total unit capacitance is not diminished.

Since the cathode's voltage capability is usually only about one volt, the electrolytic capacitor unit is limited in its steady-state reverse voltage capability to about one volt.

It has been found that in some cases transient reverse voltages in excess of 100 volts may appear on the capacitor for durations of around one millisecond with no harmful effects for thousands of cycles.

However, it is not clear what the actual cathode potential is in these cases. What is known is that extended reverse voltage for time intervals as short as one second can cause significant heating of the electrolyte and of the anode oxide.

The current drawn during these reverse voltages can easily reach hundreds of DC amperes.

In some cases electrolytic capacitors can be constructed with formed cathodes, in order to allow voltage reversal without damage.

The drawbacks to such construction are reduced total capacitance, since the anode and cathode are in series, and reduced energy density, due to the decreased capacitance and increased mass from the heavier, formed cathode [3].

4.4 - Oxide layer

Electrolytic capacitors use a chemical feature of some special metals, before called "valve metals". Applying a positive voltage to the anode material in an electrolytic bath forms an insulating oxide layer with a thickness corresponding to the applied voltage.

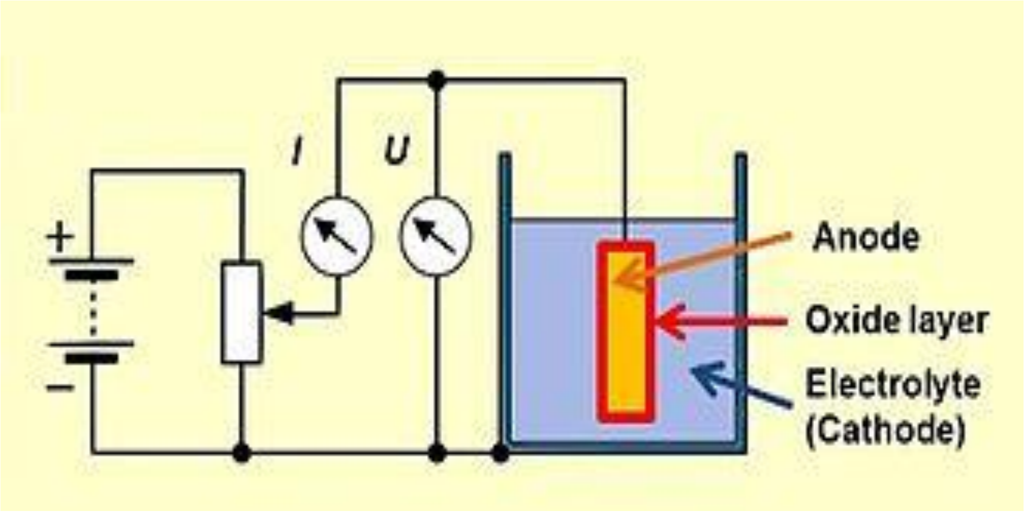

Fig. n°7: Basic principle of anodic oxidation

This oxide layer acts as the dielectric in a normal electrolytic capacitor. After forming a dielectric oxide on the rough anode structures, a counter-electrode has to match the rough insulating oxide surface. This is provided by the electrolyte, which acts as the cathode electrode of an electrolytic capacitor [29].

Electrolytes may be "non-solid" (wet, liquid) or "solid". Non-solid electrolytes, as a liquid medium that has an ion conductivity caused by moving ions, are relatively insensitive to voltage spikes or current surges. Solid electrolytes have an electron conductivity, which makes solid electrolytic capacitors sensitive to voltages spikes or current surges.

The anodic generated insulating oxide layer is destroyed if the polarity of the applied voltage changes [30].

Every electrolytic capacitor in principle forms a "plate capacitor" whose capacitance is greater: in practice, the larger the electrode area and the permittivity, and the thinner are the thickness of the dielectric. The capacitance is proportional to the product of the area of one plate multiplied with the permittivity, divided by the thickness of the dielectric.

Electrolytic capacitors obtain their large capacitance values by a large area and small dielectric thickness.

The dielectric thickness of electrolytic capacitors is very thin, in the range of nano-meters per volt, but the voltage strengths of these oxide layers are quite high. All etched or sintered anodes have a much higher surface compared to a smooth surface of the same area.

This increases the capacitance value by a factor of up to 200 for aluminium electrolytic capacitors [31].

Dielectric constant of aluminium oxide is: $\varepsilon = 8.5$.

4.5 - Paper Separator

Generally, an aluminium electrolytic capacitor is constructed by interleaving a paper separator between an anode aluminium foil and a cathode aluminium foil and winding them into a capacitor element, impregnating the capacitor element with electrolyte, placing it in a case, and then sealing it closed and aging it.

The main role of the separator in the aluminium electrolytic capacitors is the isolation of the electrodes films and retaining the electrolyte. Indeed anode and cathode foils must be protected from direct contact with each other because such contact, even at relatively low voltages, may lead to a short circuit. In case of direct contact of both foils the oxide layer on the anode surface gives no protection. A spacer or separator made of a special highly absorbent paper with high purity protects the two metal foils from direct contact. This capacitor paper separator also serves as a reservoir for the electrolyte to extend the lifetime of the capacitor. For these reasons electrical insulation is required for the material of the separator, and hydrophilic and lipophilic properties are required for retaining various type of electrolyte.

As it is necessary for the separator for an aluminium electrolytic to retain electrolyte, films that cannot impregnate electrolyte inside such as a polyethylene film, or polypropylene film, and films that dissolve electrolyte such as polyvinyl alcohol film, cannot be used as the separator.

Cellulose has these properties, and therefore electrolytic paper, which is cellulosic paper, is used as the separator for electrolytic capacitors.

The paper separator for an aluminium electrolytic capacitors requires dimensional stability and chemical stability at temperatures of 100°C or higher.

Separator paper is mainly composed of natural cellulose fibre and its thickness is generally from 20 µm to 90 µm.

Paper separator thickness and type are selected according to product impedance and rated voltage (for example it is up to 100 V between 30 and 75 µm).

High density and thick paper tends to be used for products with a high rated voltage, low density paper is selected for low impedance products.

For higher voltages, several layers of paper (duplex paper) are used to increase the breakdown strength. The two pictures show enlarged photograph of separator paper for low and high voltage. Low voltage separator is made of relatively thin and round shaped fibres for the purpose of low impedance (low ESR). In contrast, high voltage separator is made of flattened fibres to maintain high withstand voltage.

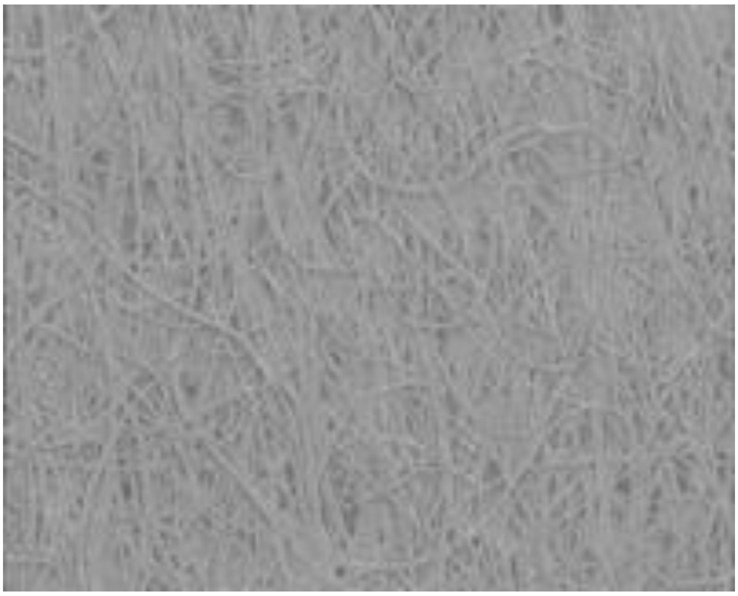

Fig. n°8: Kind of separator paper for low-voltage

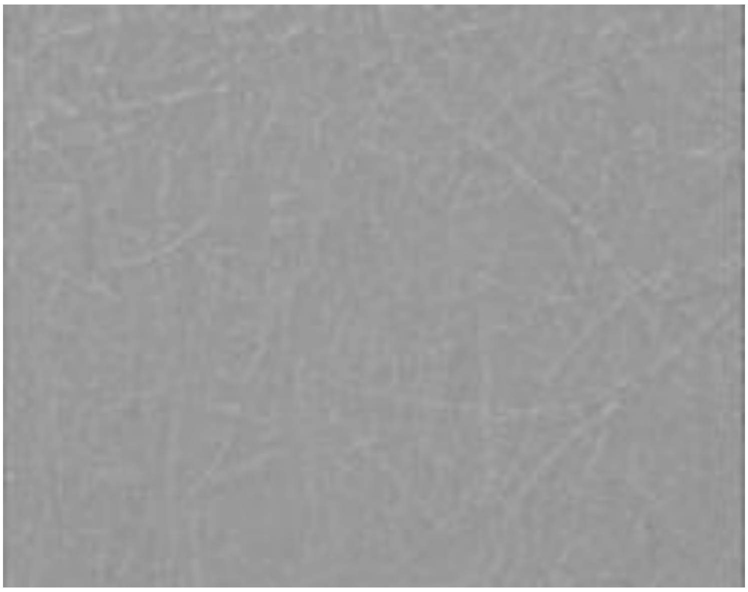

Fig. n°9: Kind of separator paper for high-voltage

A cellulose solution is obtained by dissolving cellulose in an amine oxide solvent, then it is formed in a film form, and the resulting cellulose solution is immersed in water or a poor solvent of the amine oxide solvent, so as to coagulate and regenerate the cellulose.

The regenerated cellulose is washed with water to remove the amine oxide solvent, and then dried, thereby obtaining a cellulose film that is thin, uniform, and dense and has few impurities.

In the case of medium and high voltage aluminium electrolytic capacitor, electrolytic paper having sufficiently high density and thickness to maintain the short circuit resistance characteristic is used. The higher the working voltage, the higher the risk of short circuit. Therefore, high density electrolytic paper separator of one ply with a density of 0.70 to 1.00 g/cm^3 in used.

To obtain high density paper separator, without any pinholes, it is necessary to use the “Fourdrinier Machine” that forms a raw material obtained by strongly beating or highly refining fibres, or electrolytic paper of two-ply made by layering and combining high density layers on a paper spacer making machine, which are formed by layering paper using a cylinder machine).

That paper spacer is made by dispersing fibres in water, forming fibre material on a paper making wire mesh. Thereby, the more the fibres are refined so as to further fragment the fibre diameter, more uniform and dense fibre material could be formed.

Electrolytic paper also has a limit to thinning. In the paper making process, on a paper making wire mesh, water filtering rate becomes slower as many fine fibres fall through the wire mesh during initial water removal and gradually form fibre mat, and after the middle stage of the water removal process, many fine fibres yield a wet paper, thereby gradually forming dense fibre mat [32].

A raw material having a large ratio of fibres with small diameters resulting from high refining needs to be used in order to make thin paper, since thickness of the paper depends on diameters of the raw material fibres and how many are layered.

The density of paper is measured by the following formula:

$$\text{Density (g/cm}^3\text{)} = \text{basis weight (g/m}^2\text{)} / \text{thickness (}\mu\text{m)}$$

Thus, when paper having the same basis weight becomes thinner, density increases.

Fig. n°10: Roll of virgin dechlorinated paper separator

4.6 - Electrolyte solution

The electrolytic capacitor got its name from the electrolyte, the conductive liquid inside the capacitor. As a liquid it can be adapted to the porous structure of the etched anode and the grown oxide layer with the same shape.

An electrolyte always consists of a mixture of solvent and additives to meet given requirements. The main electrical property of the electrolyte is its conductivity, which is physically an ion-conductivity in liquids. In addition to the good conductivity of operating electrolytes, various requirements are, among others, chemical stability, higher flash point, chemical compatibility with aluminium, low viscosity, low environmental impact and low costs. The electrolyte should also provide oxygen for forming and self-healing processes, and all this within a temperature range as wide as possible. This diversity of requirements for the liquid electrolyte results in a wide variety of proprietary solutions.

The electrolyte that it is used to carry out the impregnation test is the working electrolyte in the capacitor.

It should be highly conductive and operate over a wide temperature range with high boiling point, low freezing point, and long lifetime [33].

Specifically analysis focuses only on the electrolyte which has guaranteed the best impregnation: moreover this electrolyte should have low viscosity to ease processing, should be chemically inert for low leakage current, and should be environmentally friendly, non-toxic, self-extinguishing in case of fire, and relatively inexpensive.

These many requirements have made it difficult to find a unique, effective electrolyte solution and moreover, thousands of patents for non-solid electrolyte systems exist, none of which is perfect [6].

The most important electrical property of the operating electrolyte for e-caps with low equivalent series resistance (ESR) is its charges conductivity, which is provided by ion-conductivity. An electrolyte always consists of a mixture of solvents and additives to achieve the desired compromise among the many different and conflicting attributes. The additives are acids or bases that make the electrolyte conductive, but this must be achieved without the electrolyte becoming excessively aggressive chemically to aluminium and its oxide; for example the use of halogens is not recommended.

Early e-caps production indeed suffered from poor aluminium purity, poor cleanness during manufacturing, and excessively aggressive electrolytes, so the oxide layer was not stable.

As a result, the early development of aluminium electrolytic capacitors is plenty of episodes concerning corrosion, increased leakage currents, and ruinous explosions.

The main issues today in the electrolytic capacitors technology are no longer quality and reliability but diversification resulting from the growing demand for specific capacitor characteristics in a wide range of industries, such as low leakage current, low ESR for high ripple current capability, higher temperature operation, and/or longer life.

As a result, capacitor characteristics are being customized for specific applications, mainly through modification of the working electrolyte.

Currently used operating electrolytes are nearly free of halogens and, if necessary, contain inhibitors to water-based corrosion.

In a very rough simplification, operating electrolytes can be divided into three groups:

- Electrolytes based on ethylene glycol and boric acid. These borax electrolytes are standard electrolytes, long in use, and with a low water content: between 5 and 20%. They work at a maximum temperature of 85°C or 105°C in the entire voltage range up to 600 V. Even with these capacitors, the aggressiveness of the water must be prevented by appropriate measures, using for example additives in electrolytic solution.

- Anhydrous electrolytes based on organic solvents, such as dimethylformaldeide (DMF), dimethylacetamide (DMA), or γ-butyrolactone (GBL).

The capacitors with these organic solvent electrolytes are suitable for temperature ranges from 105°C, 125°C or 150°C. They have low leakage current values and have very good long-term capacitor behaviour.

- Water based electrolytes with high water content: up to 70% water, for so-called "low-impedance", "low-ESR" or "high-ripple-current" electrolytic capacitors with rated voltages; up to 100 V for low-cost mass-market applications. The aggressiveness of the water for aluminium have to be prevented with suitable additives [6].

Since the amount of liquid electrolyte during the operating time of the capacitors decreases over time through self-healing and by diffusion through the seal, the electrical parameters of the capacitors may be adversely affected, limiting the during of service life or lifetime of wet electrolytic capacitors [34] [35].

4.7 - Tabs

Tabs are strips of aluminium which make contact between the conductive plates and the connection terminals in the header.

There may be several tabs connected to each of the plates. Each tab is cold-welded or staked along the width of the anode and cathode foils.

The tab paths are generally run from the capacitor section to the terminals in a way which keeps the inductance low and prevents tabs of the opposite polarity from coming in contact with one another or the case during movement and vibration of the capacitor unit.

The tabs are spot welded to the underside of the terminals in the header assembly. Tab material is not etched, but is formed to a high voltage prior to its assembly into a capacitor.

Optimum tab placement along the foil is considered to be the placement that minimizes power loss due to the metal foil resistance.

This placement leads to equal spacing from each tab to the one nearest it, and half of the inter-tab distance is provided between the outermost tabs and the foil ends.

For high voltage capacitors, the tab resistance and metal foil resistance are quite small compared to the oxide and electrolyte resistance [3].

4.8 - Package

The can into which the capacitor section is placed is made of 1100 alloy aluminium, which is of around 99% purity. For 25 to 50 mm (equivalent to one-inch to two-inch) diameter of capacitors, the wall thickness is 0.022 inches.

A butyl rubber gasket is placed on top of the header before the spinning operation, in which the case opening is folded over and pressed into the gasket, forming an effective seal of the system. The package is at the same potential as the electrolyte and cathode during capacitor operation, so when electrolytic capacitors are connected in series, it must be taken cure to insulate the cases from one another. Although the aluminium electrolytic capacitor case is at the cathode potential, it may not be used for the negative electrical connection because of high electrolyte resistivity and the long effective path from the cathode to the can. If the electrolyte were of much lower resistivity, eliminating the cathode and using the can instead might be a possibility.

A safety vent is provided in capacitors so that the capacitor may relieve excessive pressure build-up in a controlled manner. This occurrence is known as venting, and is considered a failure mode. The vent may be installed as a rubber plug in the header or as a die-set slit impression in the can wall. After a capacitor vents, the electrolyte may evaporate out until the capacitance decreases [3].

CHAPTER 5

Materials and methods used in laboratory

5.1 - General explanation of experimental work

After providing a general overview of the world of electrolytic capacitors and specifically on aluminium electrolytic capacitors, now we shall analyse a specific capacitor, produced by the Italian company Itelcond, and the production process that leads to the formation of the final device. In particular, the analysis are focused on the materials used for the production of this capacitor, on the impregnation process, on physical processes that occur during the impregnation and finally on the electrical properties of these devices once finished.

The impregnation starts testing the production method used in the company, after which is possible to change some parameters of this production process with the aim of reducing impregnation times or temperatures, obtaining devices with electrical properties and similar resistances compared to those produced in the company with the standardized process of impregnation.

5.2 - Itelcond Company

Itelcond was founded in November 1976 and since then the company policy has been devoted to the production of capacitors for the professional, industrial, and telecommunication domain.

Itelcond company deals with the production of aluminium electrolytic capacitors for professional applications when high voltage and good capacity is required.

The product range goes from the large screw capacitor to the small capacitor for printed circuit, always in the professional field. They collaborate with companies that build electronic equipment, alternative energy (solar - wind), UPS, inverter, motor control, electronic medical equipment.

The production lines have been continuously devoted to the manufacture of large capacitors units, with screw terminals for fitting in many different electronic equipment, with brackets or with mounting stud.

Fig. n°11: Aluminium electrolytic capacitor produced by Itelcond

During the first forty years from foundation, the company has dedicated a lot of energy to the reliability of the product, these years of research, conducted with the support of Italian universities, have made possible to reach an excellent reliability on the entire range of our products.

The production is constantly evolving with the most up-to-date automation for the production of increasingly reliable capacitors and these updates make it possible to adapt to the most advanced international standards for productivity and quality.

During the last years this type of capacitors widened its usage in many fields as power supply: UPS, welding and magnetizing machines, equipment for railway applications.

Therefore, Itelcond’s production has been widened: new series have been added to the existing one.

Itelcond company has chosen to manufacture units with higher working voltage paying special attention to the range of high voltages (350 volts and up), high capacitance-volume ratio and high ripple current [36].

5.3 - Materials and methods

In this chapter, introductory to the experimental part, materials and methods that have been used in this thesis work are going to be pointed out, each of them with a brief description.

This chapter represents a collection of information preliminary to the laboratory activity carried out.

The following is a list and an explanation of the materials, equipment and main methodologies used to produce and test the sample.

The aim is to provide a precise description of both the properties of the materials and the principles underlying the equipment as well as their use, in order to make available all the necessary indications for the evaluation of the properties of the samples made.

5.4 - List of materials

The materials supplied by Itelcond are:

- Three different impregnating electrolyte solutions (A55m, A55p, H2000).
- Three different sheets of paper separator.
- Aluminium electrodes (anode and cathode).
- Capacitors composed by an aluminium foil and paper, wrapped, not yet impregnated and sealed.

Using starting materials, the impregnation process is replicated with the separator papers and the electrolyte solutions, at different temperatures and operating conditions, in order to find the best combination in terms of quantity of electrolyte left impregnated after drying the sample in the oven.

Characterization tests were carried out on the specimens obtained in order to have quantitative and qualitative responses on the impregnating solute remaining in the paper spacer volume.

Finally, electrical characterization test (charge test) was performed to measure the electrical properties (capacitance and resistance) of the capacitors impregnated in laboratory.

5.4.1 – Electrolytes solution

Since its foundation Itelcond never used in its electrolytes dangerous formulation or potentially poisonous chemicals [36]. Therefore all electrolytes are free from:

- Dimethylformamide (DMF)
- Dimethylacetamide (DMAC)
- Polychlorinated byphenil (PCB)

The solutions supplied by Itelcond are used in impregnation process and characterized during the experimental work in laboratory.

These are of the type borax/glycol electrolytes: these solutions are composed of a mix of mono-ethylene glycol, water and borates, as sodium penta-borate.

The three solutions, formulated by Itelcond and sent to us are classified as follows:

Solution a: A55m

Solution b: A55p

Solution c: H2000

The A55m solution is obtained by dehydrating the A55p solution, in practice a small percentage of water is subtracted from the solution A55p in order to obtain the first solution A55m, through boiling under vacuum. In this process about 10 litres of water are extracted on 200 kg of solution from A55p liquid in order to obtain solution A55m.

It must be said that in this case we have the same electrolyte solute composition and the difference between the two solutions is the different viscosity, due to the different content of water inside the electrolyte.

As for the third solution, it is again a mixture of water, glycol and borates as well, but in this case the electrolyte has a lower solute content, probably due to higher water and glycol content in the solution.

5.4.1.1 - Characterization tests performed on the electrolyte

The first tests carried out on these solutions are qualitative tests and specifically are thermogravimetric and rheological analysis.

These tests were carried out to verify the nature and the rheological behaviour of the three different electrolytes. This is important because the nature of the electrolyte influences the electric properties of the final device [37].

Through these characterizations, the impregnated sample is compared with the sample already analysed before the process.

5.4.1.2 - Thermogravimetric test carried out on H2000 solution

Thermogravimetric analysis show a decrease in weight of the analysed specimen (due to evaporation) depending on temperature.

From this graph we can infer the structure of H2000 electrolyte: immediately after 100°C the decrease in weight starts due to the loss of water, the narrow peak at 400°C in the DTG curve is an indicator of the decomposition temperature of the organic compounds (as glycols or alcohol).

The remaining solute, which has not be affected by heat treatment, is a conductive salt, formed by borates.

H2000 solution

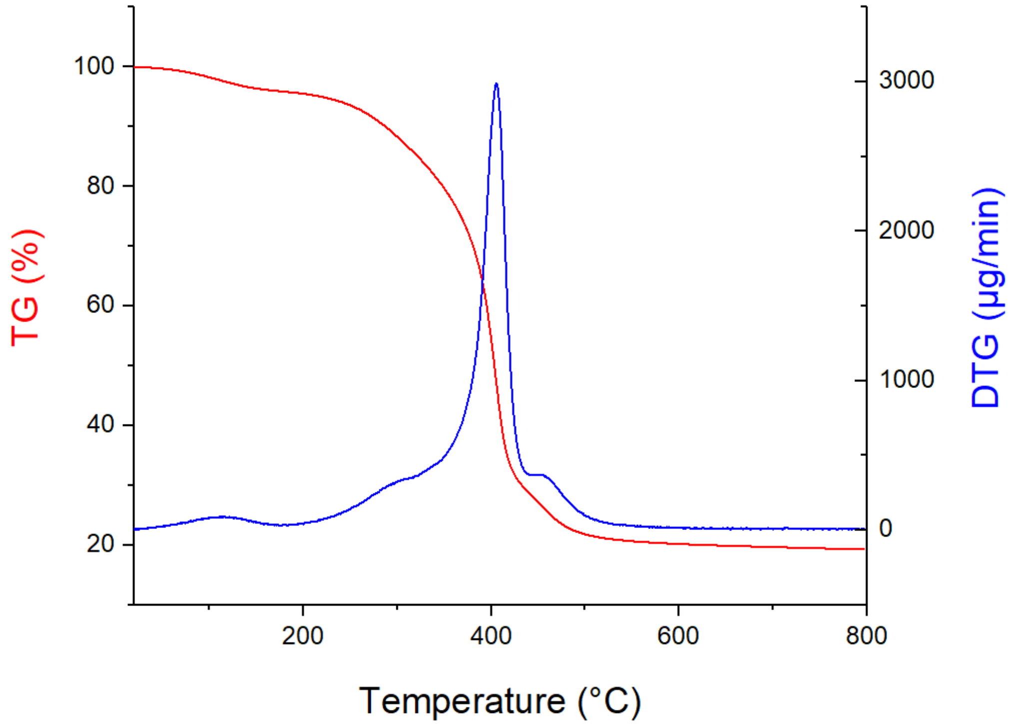

Fig. n°12: Thermogravimetric analysis of H2000 solution

5.4.1.3 - Rheological test

After the thermogravimetric tests, rheological tests have been carried out on these electrolyte solutions, at a constant temperature first, investigating the viscosity variation a function of the applied shear rate.

Then the tests are carried out at constant applied stress, and such measurement is useful to evaluate the variation of viscosity due to the temperature increment.

Solution A55m:

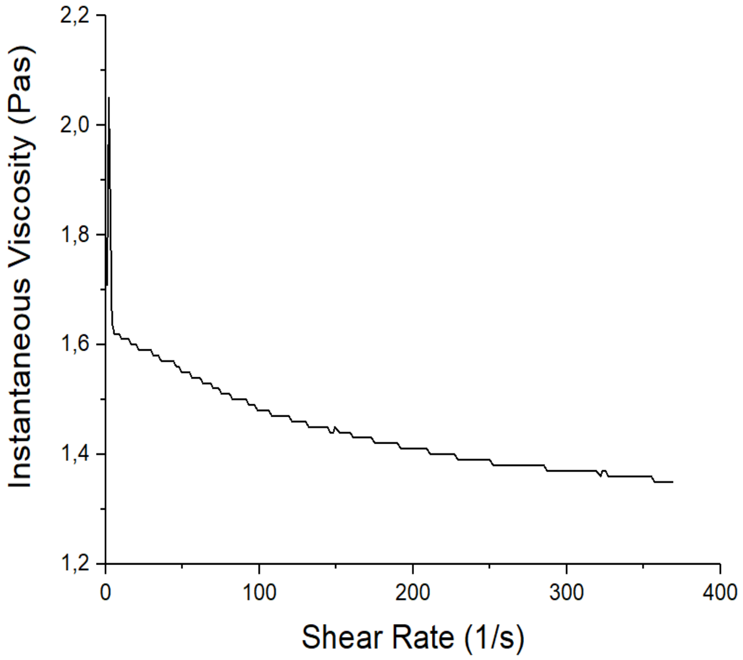

Fig. n°13: Viscosity curve of solution A55m (at constant temperature)

Solution A55p:

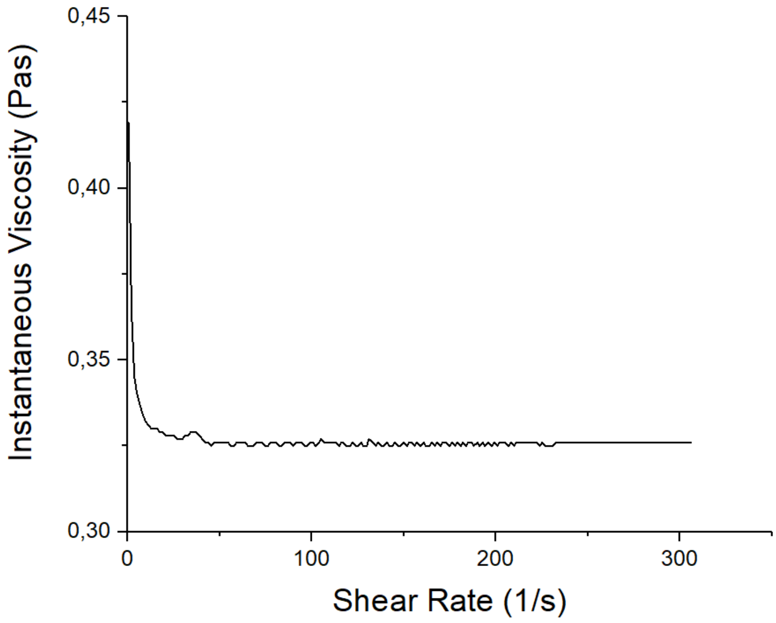

Fig. n°14: Viscosity curve of solution A55p (at constant temperature)

Solution H2000:

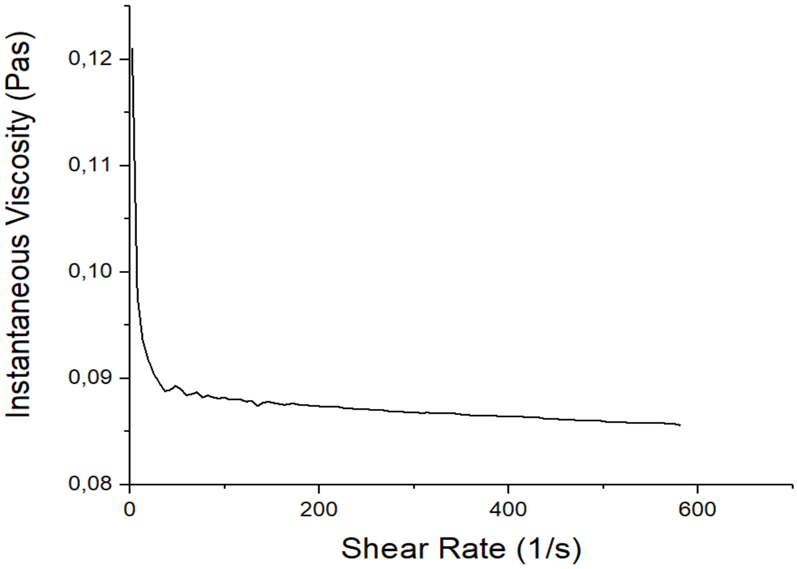

Fig. n°15: Viscosity curve of solution H2000 (at constant temperature)

The rheological tests of the three solution samples were performed at 25°C; viscosity follows the trend:

Viscosity of A55m > viscosity of A55P > viscosity of H2000

This trend can be explained by the nature of the electrolytic solution, the solution A55m has the same chemical composition of solution A55p but with a lower water content, the solution H2000 is tuned with a low solute content to reduce the viscosity.

Upon increasing the shear rate, the viscosity of solution stabilizes around a constant value showing a Newtonian behaviour, we could see from these plots that the value for the first solution tested (A55m) is considerably higher than the other two.

Instead the third solution (H2000) has a lower viscosity, about one magnitude order in respect with the other two electrolyte solutions.

Following, the results of tests performed at different temperature are reported.

Solution A55m:

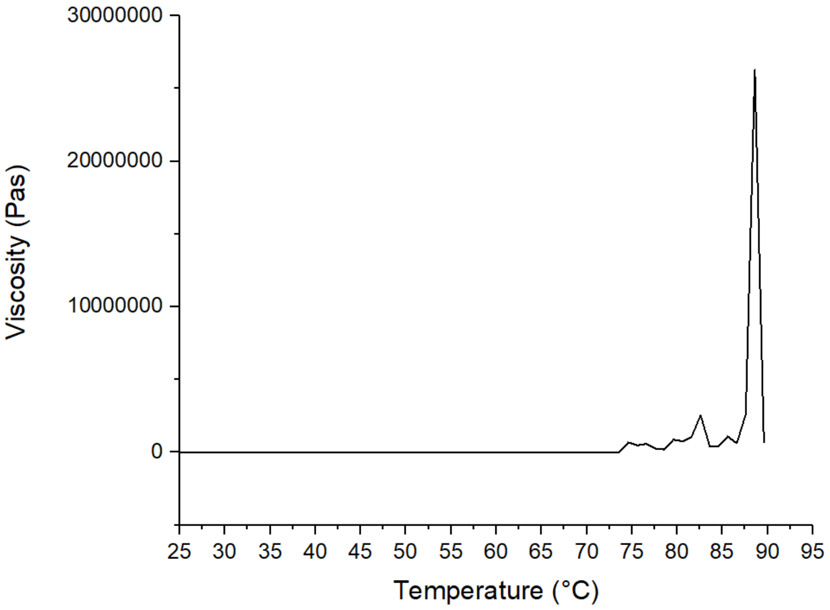

Fig. n°16: Viscosity curve of solution A55m (at constant shear rate)

Solution A55p:

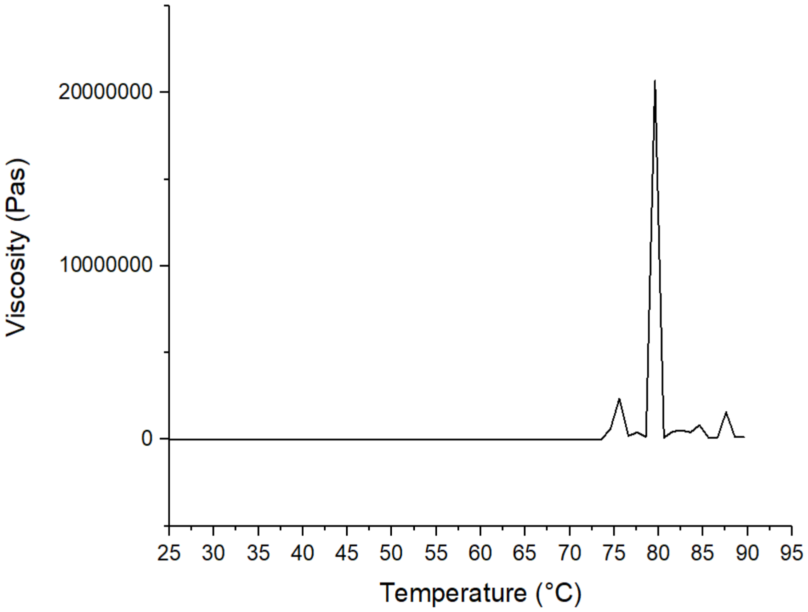

Fig n°17: Viscosity curve of solution A55p (at constant shear rate)

Solution H2000:

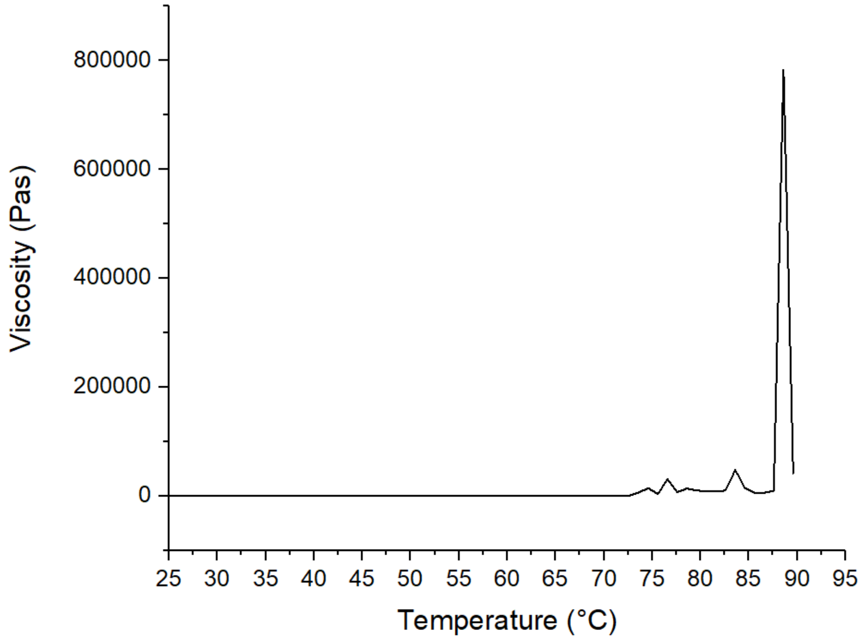

Fig. n°18: Viscosity curve of solution H2000 (at constant shear rate)

In this test the applied stress shear is kept constant and the temperature range is from 25°C to 90°C.

From these graphs it could be seen that until 85°C the viscosity remains constant, but at higher temperatures it starts to increase as shown by the narrow peaks in the plots.

The increase of viscosity can be attributed to the evaporation of water in the solutions.

In the case of solution A55p the increase of viscosity happens at a lower temperature with respect to the other solutions (the peak is placed about 80°C).

5.4.1.4 - Viscosity effect on aluminium electrolytic capacitor capacitance

We know that according to chemical behaviour of the employed ionic liquids the electrical properties of the final capacitor device may change.

In particular, it has been found that the performance of the ionic liquid electrolytes may be related to the solution viscosity and ion size whilst the electrolyte equivalent series resistances produced a linear relationship with viscosity.

The variation in electrical properties of the capacitors that have been analysed is the variation of capacitance with ionic liquid electrolyte.

It cloud be assumed that an electrolyte should possess the lowest possible viscosity along with a small ion size.

In order to allow a comprehension of analysis for the capacitive performance of different ionic liquid electrolytes, the ions can be termed as ‘‘soft’’ or ‘‘hard’’ ions depending on where the delocalised charge is situated: as a ‘‘soft’’ ion the charge increases, thus increasing the dielectric constant as the ion-ion attraction is lower.

Conversely in a ‘‘hard’’ cation, due to the stronger charge the dielectric constant decreases.

Consequently, the ionic liquid utilising this cation exhibits stronger ion-ion interaction and a lower $\varepsilon_{(r)}$ due to lower volume of dissociated ions.

The ionic liquid with the lower capacitance is the one with the higher viscosity, the poor capacitance performance of that electrolyte could be attributed to the higher viscosity, reducing the mobility of the ions and resulting in a weaker interaction between the electrode and electrolyte ions.

Viscosity may influence the performance of capacitor also because impregnation is strongly dependent on viscosity.

Viscosity, however, is not the only factor that influences the conductivity of the electrolytes, ionic size has to be taken into account.

Ionic size must be taken into account because if the ion size is too large with respect to the size of pits forming during the etching process, carried out on the anode, the entrance in the hole is not allowed. In this case the electrolytes could not wet perfectly the aluminium surface causing a non-perfect contact between the dielectric (the aluminium oxide layer) and the cathode.

The best capacitive performance was obtained for the electrolyte that better combines the ‘‘soft’’ cation with the small ‘‘weakly coordinating’’ anion. This combination, based on the theory given above, gives rise to the ionic liquid with the apparent highest $\varepsilon_{(r)}$ among those tested in the study.

The small ion size coupled with the lower viscosity and relatively high conductivity results in the best performance [37].

5.4.2 - Paper Separator

Paper separators used by Italcond are virgin, dechlorinated paper [36]. We tested three different types of paper separator supplied by the company.

- Paper separator a: rigid paper (20 µm)
- Paper separator b: soft paper (40 µm)
- Paper separator c: soft paper (50 µm)

Dismantling a capacitor supplied by Itelcond we realized that the assembly mechanism involves the coupling of two different paper separators wrapped together (one paper is more rigid and has higher density, while the other one is thicker and softer).

The capacitor is composed by rigid paper in contact with the cathode and soft paper in contact with the oxide surface formed on the anode.

This duplex structure is placed between the two aluminium plates before being rolled up.

The first measure carried out on these paper samples were aimed at evaluating their density in grams by volume, as it is the same measure way that we use to calculate the quantity of electrolyte remained trapped.

- Paper separator a: 0.978 g/cm^3
- Paper separator b: 0.734 g/cm^3
- Paper separator c: 0.687 g/cm^3

The analysis of the rigid paper separator before impregnation by thermogravimetric test and IR spectroscopy test is for evaluating the chemical-physical properties of the paper.

The rigid paper separator has been chosen because it is the one with the highest density: the high density of the paper is convenient for measurements as problems with measurement due, for instance, to humidity, are less evident.

In this way we get some graphs that we can then compare with the graphs obtained from the analysis of impregnated specimens.

It is possible to check how the electrolyte solution changes the chemical-physical nature of the impregnated paper.

5.4.2.1 - Characterization of rigid paper separator

The rigid paper separator is analysed by thermogravimetric test and IR spectroscopy analysis.

5.4.2.2 - Thermogravimetric analysis of rigid paper separator

From the graph, we can see there is a great weight loss for the paper between 280 °C and 360 °C: in this temperature range the cellulose will tend to burn reducing the weight of the paper specimen.

Further information can be obtained from the first derivative of this loss in percentage (DTG) measured in µg/min.

The narrow peak in the derivative of DTG curve correspond to abrupt loss in weight, due to the paper separator evaporation.

At the end of the process it is possible to note a residual weight around 20% of the initial.

Left-shift of the narrow peak in thermogravimetric analysis of impregnated paper separator samples must be expected, due to addition of liquid electrolyte in the volume of paper separator.

Therefore the sample starts to loses weight at lower temperature with respect to paper separator TG analysis.

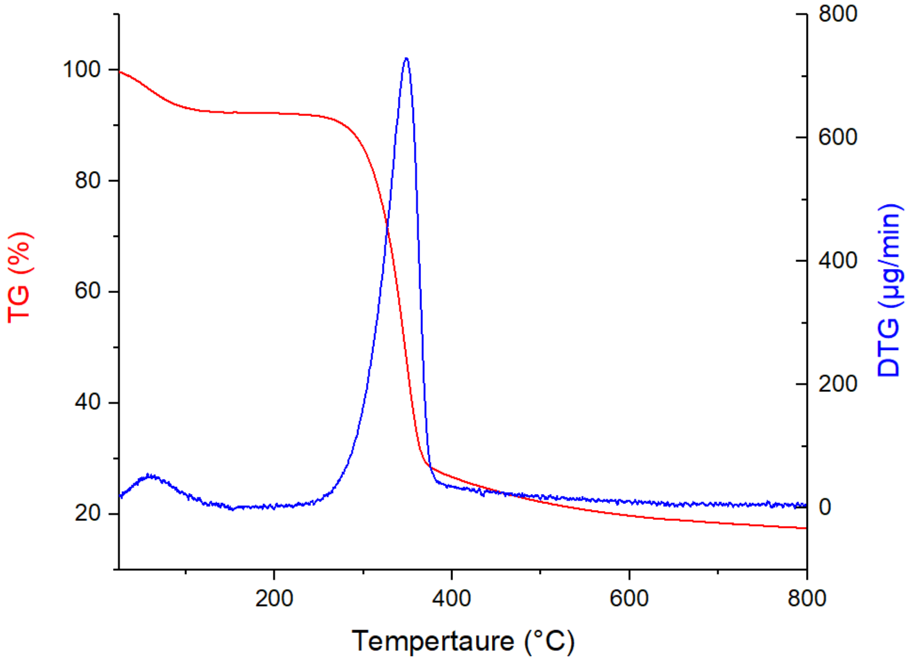

Fig. n°19: Thermogravimetric plot of rigid non-impregnated paper

5.4.2.3 - IR spectroscopy of rigid paper

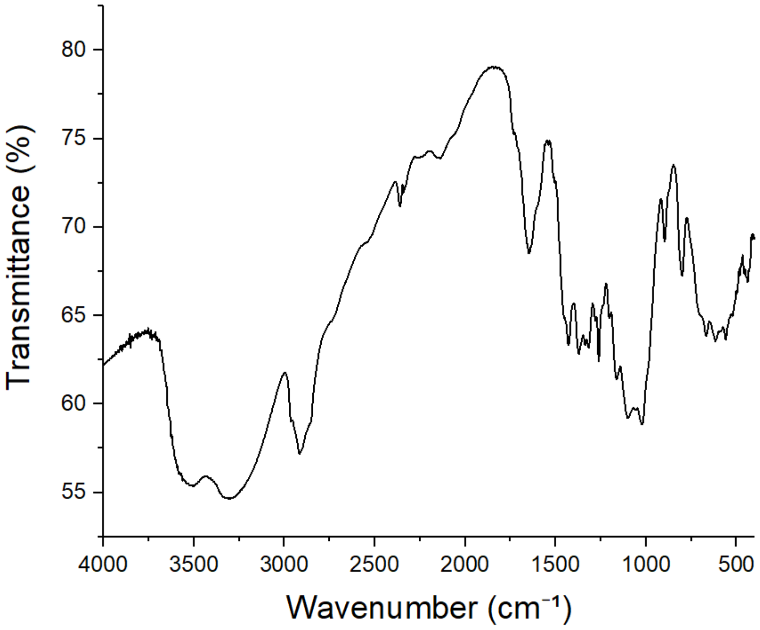

Fig. n°20: IR spectroscopy graphic of rigid non-impregnated paper separator

From the IR spectroscopy graph we observe that peaks are the same of the peaks that characterize a cellulose infrared spectrum, as it is found in literature. Peaks of cellulose's IR spectroscopy graph are due to O-H vibration at frequency about 3000 cm^{-1}, other significant peaks comes from the CH-OH, C-O, C-OH and C-Cl vibration. These other significant peaks could be found under 1500 cm^{-1} frequency wavenumber [38]. After the impregnating process and drying, it is possible to characterize the impregnated samples in order to compare them with the previous analyses, carried out on the sample made of virgin paper.

5.4.2.4 - Porosimetry test

Porosimetry test is performed to estimate the total amount of pores and pores distribution size in different paper separators, in order to know the amount of electrolyte trapped during impregnation process.

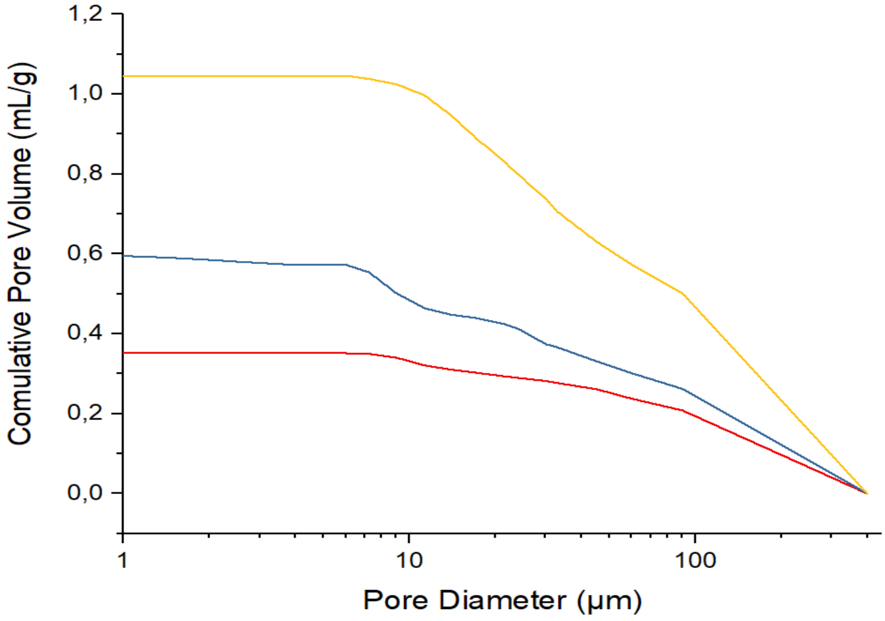

Fig n°21: Cumulative pore volume of paper separator: a, b and c

The yellow line in the graph shows the cumulative pore volume of the softer and thicker paper separator, the red line represents the rigid paper separator and the blue one is correlate to the paper separator b (show an intermediate characteristic between the other two).

Porosimetry tests show that the thinnest paper, as it is the one with the highest density, is the one showing the lowest porosity; the other papers reported similar values.

Therefore we expect less impregnation value on the thinner separator paper due to the smaller volume of pores available.

The tests of measurement of differential pore volume are shown below:

Rigid paper separator a:

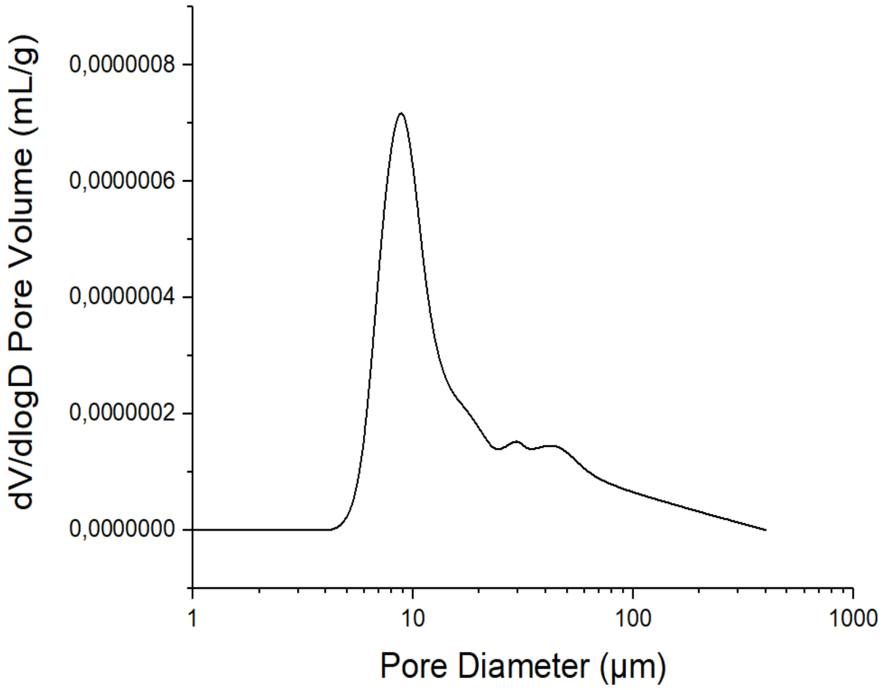

Fig. n°22: Differential pore volume of rigid paper

Soft paper separator b:

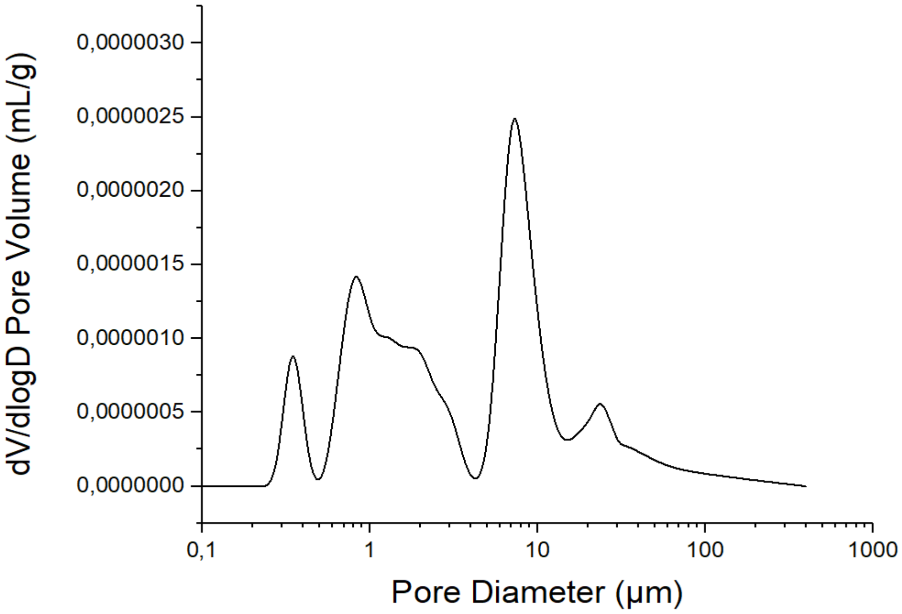

Fig. n°23: Differential pore volume of separator paper b

Soft paper separator c:

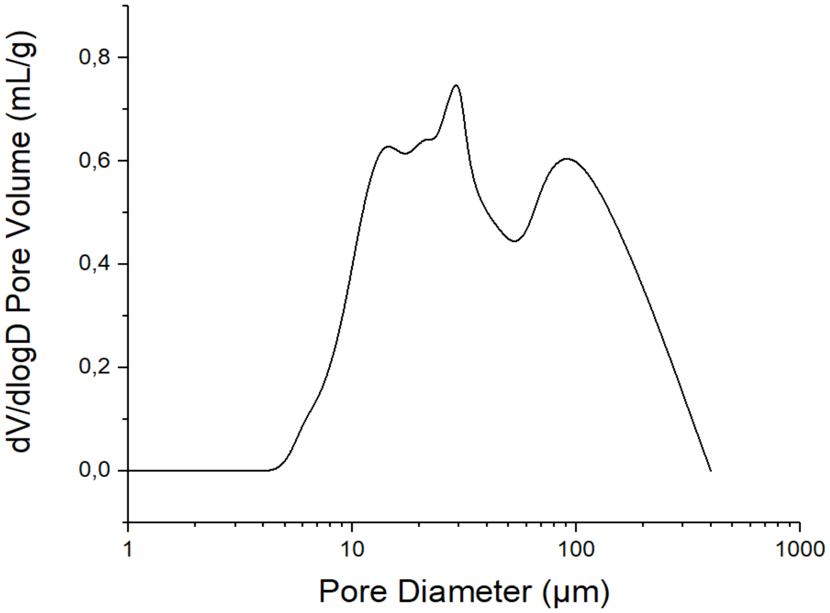

Fig. n°24: Differential pore volume of separator paper c

5.5 - Methods

In this section of the thesis, all methods and equipment used during characterization work will be described in detail.

In particular thermogravimetric and IR spectroscopy analysis have been performed before and after the impregnation tests, as well as rheological and porosity test on starting materials.

5.5.1 - Thermogravimetric analysis

Thermogravimetric analysis (TG) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature with constant heating rate, or as a function of time with constant temperature and/or constant mass loss.

Thermogravimetric analysis provides information about physical phenomena, such as second order phase transitions, including vaporization, sublimation, absorption and desorption.

Likewise, it provides information about chemical phenomena including chemisorption, dehydration and decomposition.

The TG instrument continuously weighs a sample as it is heated to an imposed temperature. As the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass change can be measured.

Fig. n°25: Instrument used for TG analysis

Results finally are plotted with temperature on the X-axis and mass loss on the Y-axis.

The data can be adjusted using curve smoothing and first derivatives are often also plotted to determine points of inflection for more in-depth interpretations.

The final result is a curve that shows the absolute or percentage variation of the mass against the temperature or time.

Thermogravimetric curves are characteristic of a specific material or chemical compound since weight variations are due to the formation and break of chemical and physical bonds at determined temperatures. TG tests can be done under nitrogen or air atmosphere that are respectively inert and reactive.

Temperature range normally goes from room temperature to 1200 °C: in our case we have to analyse paper separator and electrolytic solution so our temperature range starts from room temperature and ends at 800°C.

We analyse with this technique papers separator samples before and after the impregnation process and the single electrolyte.

5.5.2 - Rheological tests

Viscosity is a liquid’s resistance to flow and generally is measure in relation by time and temperature.

The viscosity can be evaluated in vary ways, in order to perform rheological characterizations of the electrolyte solution utilised, a Stresstech 500 rotational rheometer was used. Through this instrument it is possible to derive the dynamic viscosity trend when the applied shear rate varies.

The rotational rheometer is an instrument composed of a movable upper plate with variable geometry (specifically a circular flat shape with a diameter of 40 mm) and a lower fixed plate.

Between the two surfaces a fluid layer is placed with a determined thickness of 0.5 mm.

Subsequently a variable force (torque) is applied to the movable plate in such a way as to generate a rotational movement.

By intervening with a modulation of the applied torque it is possible to vary the rotation speed and consequently the shear rate.

By measuring the opposing resistance from the fluid to the movement it is possible to calculate the viscosity value corresponding to the shear rate value imposed by the velocity.

5.5.3 - Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals.

Samples may be solid, liquid, or gas. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum.

When an infrared photon is absorbed by a molecule, it passes from its fundamental vibrational state to an excited vibrational state. In a typical infrared spectrum in the X – axis there is a scale of frequencies expressed in wave number, that represent quantity of waves per centimetre, and in Y-axis the percentage of transmittance. If a material is transparent to infrared radiation, its spectrum will be presented as a line parallel to the abscissa axis. If a material is not completely transparent, absorptions and therefore transitions between vibrational energy levels will occur. In this second case the recorded spectrum will be characterized by a series of peaks of varying height for each transition.

From what has been said it is possible to verify that the greater the strength of the bond, the greater the frequency of vibration for a given vibrational level, while the heavier the atoms, the lower the vibrational frequency.

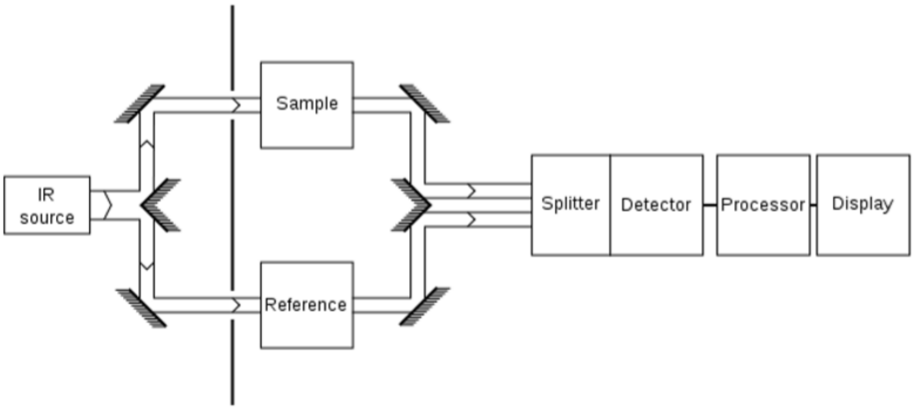

Fig. n°26: Diagram of a spectrometer

An FT-IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis versus frequency or wavelength on the horizontal axis. Typical units of frequency used in FT-IR spectra are reciprocal centimetres (cm-1, sometimes called wave numbers). Units of IR wavelength are commonly given in micrometres, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier transform infrared (FT-IR) spectrometer. The following figure shows the instruments used in laboratory to carry out the tests:

Fig. n°27: Spectrometer used in laboratory

A measurement, in order to be performed, needs a correct preparation of the sample. The material to be analysed must grinded into powder and inserted into a K-Br pellet. Also KBr needs to be reduced into powder, this operation should be fast because K-Br is a very hygroscopic compound and atmospheric humidity may affect the pellet. For the production of the pellet, proper amounts of powders of K-Br and of the sample to be analysed are mixed together and compressed under a pressure of 10 ton cm^2 for 10 minutes. Then the sample is ready to undergo the test.

5.5.4 - Porosimetry

The term "porosimetry” is often generically used for a series of measurements that include: pore size, volume, density, and other characteristics related to the porosity of a material.

Porosimetry is an analytical technique used to determine various quantifiable aspects of a material porous nature, such as pore diameter, total pore volume, surface area, and bulk and absolute densities.

The technique involves the intrusion of a non-wetting liquid (often mercury) at high pressure into a material through the use of a porosimeter.

The pore size can be determined based on the external pressure to force the liquid into a pore against the opposing force of the liquid surface tension.

The instrumentation used to perform this analysis was the Carlo Erba Porosimeter 2000 Series instruments, shown in the following figure:

Fig. n°28: Instrument used for porosimetry analysis

The relationship between applied pressure and pores size into which mercury may penetrate is expressed by a force balance equation known as Washburn's equation:

$$P \cdot D = 4\gamma \cdot cos\theta$$

Where:

- P: applied pressure
- D: diameter of the pores
- γ: surface tension of liquid; if mercury, it is 0.559 N m^{-1} at 20°C
- θ: inner contact angle of intrusion, typically around 140°

Thanks to porosimetry test, the porosity of a material can be determined.

It is generically determined as the ratio between the volume of the pores (Vp) and the total volume of the material (Vm):

$$\varphi = \frac{V_p}{V_m}$$

Porosity is a fundamental parameter to define the permeability characteristics of a material under different conditions of saturation and, consequently, it influences the electric or ionic conductivity of saturated materials.

Three types of porosity exist:

- Microporosity: pores diameter < 20 Å (D < 20 Å);
- Mesoporosity: pores diameter in between 20 and 500 Å (20 Å < D < 500 Å);
- Macroporosity: pores diameter in between 500 and 1000 Å (500 Å < D < 1000 Å).

The porosity of a material is important in understanding the formation, structure and potential use of many substances. Porosity affects its physical characteristics and consequently its behaviour in the surrounding environment. Adsorption, permeability, strength, density and other factors influenced by the porosity of any material determines the way in which it can be used.

CHAPTER 6:

Experimental work done in the laboratory: impregnation tests

6.1 - Explanation of impregnation process

The goal of these tests is to analyse the individual steps of the process of impregnation and to assess if there may be the possibility of change some parameters of the process aiming at reducing costs (thus reducing the quantity of time or the temperature in impregnation process) while maintaining the same characteristics.

Considering the scarcity of sources regarding the impregnation process, it has been decided to start soaking tests with the parameters and materials come from Itelcond company: the impregnation experiments include all the electrolytes and all the paper separators, impregnating through the method used by Itelcond.

Impregnating temperature of the standard process is 85°C degrees, with a six-cycle alternating consisting of low pressure and ambient pressure; then we reduced the temperature and the duration of the process, up to obtaining comparable samples.

At the end of the process, after drying, it is possible to evaluate which paper separators and electrolyte solutions are the most suitable for storing greater quantities of electrolyte solution in the paper after drying in the oven.

The method for impregnating these capacitors consists of dipping them rolled into a hot electrolyte bath with alternating vacuum cycles, so as to increase the diffusion and penetration of electrolytic solution through the pores of the paper; depending on the type of electrolyte different impregnation methods may exist.

The impregnation process is so important because in case of imperfect impregnation, the final device will not be able to function as a capacitor, since there would be areas of the anode not connected directly to the cathode through the electrolyte.

This is because during the impregnation the electrolyte solution must penetrate the entire volume of the paper so as to completely wet the cathode and the anode on which the etching has been done. In particular, in the anode case, we need the highest viscosity of the electrolyte in order to let the oil penetrate into all the cavities formed by the electrolytic oxidation process, so that the dielectric, the oxide, is completely in contact with the conductive solution.

We use vacuum cycles and high temperatures to optimize the impregnation process: higher vacuum values drive the electrolyte solution into the paper, higher temperature facilitate the diffusion process.

6.2 Instrumentation used in the laboratory

To perform these impregnation tests we used:

- Rotavapor Heidolph Laborota 4000:

Such tool allows us to impregnate our paper samples into a glass flask containing the electrolyte solution with controlled pressure and temperature.

The glass flask is immersed in a tank of water that is kept at the temperature set by the machine, in this way we can keep the temperature of the electrolyte constant during impregnation.

This glass flask is connected to a vacuum pump. This mechanism allows us to select and adjust at the pressure of the impregnation simply by switching the vacuum pump on and off.

Fig. n°29: Rotovapor used in laboratory

- Vacuum pump:

The vacuum pump is a mechanical device used to create and maintain a lower pressure condition than atmospheric pressure. To fulfill this purpose, the vacuum pump removes the gas contained in the vacuum chamber, the glass flask, to which the pump is connected through a rubber tube.

We use this pump to decrease the pressure inside the container where we are impregnating the papers with oil to optimize the impregnation process.

- Oven:

The oven is used after the impregnation of each single paper in order to dry the specimens. We set the oven at a temperature of 105 °C so as to eliminate the water contained in the impregnated the paper, leaving only the electrolyte in the paper volume.

After remaining for forty-eight hours in the oven, the specimens are weighed and left to rest awaiting for further analysis.

6.3 - Operating conditions

Operating conditions are set in order to simulate as closely as possible the production process of Itelcond company, then the impregnation process temperature is fixed at 85°C and process steps repeated for six alternating vacuum cycles.

Then, in order to have a complete picture of the situation we changed process parameter such as temperature and number of alternating cycles.

a) Fifteen minutes at 60 mbar and fifteen minutes at room pressure, alternated for six times.

b) Fifteen minutes cycles at 60 mbar and fifteen minutes at room pressure, alternated for three times.

Impregnation temperature:

1) Following the standard process: 85°C

2) Trying to lower the temperature: 65°C

6.4 - Impregnation process

The impregnation experiment started by filling a glass flask with the chosen electrolyte solution: this flask is attached to the Rotavapor and immersed in water at the desired temperature in order to keep the electrolyte at that temperature.

Then the paper samples are cut and their dry weight measured.

Therefore characteristics before carrying out the impregnation process can be determined and so, it is possible to measure the effectiveness of the process:

- Subtracting the weight of the sample of virgin paper by the weight of the impregnated samples we can estimate the amount of electrolyte trapped in the paper volume.
- Knowing the surface of this sample and its thickness (20 µm, 40 µm or 50 µm) it can be possible to calculate the quantity of electrolyte impregnated referred to the volume of paper (g/cm^3).

After being reduced to the desired size weighted the three different paper samples are completely immersed in the glass flask where there is the electrolyte solution at the desired temperature.

After the glass flask is inserted into the water at the set temperature, the impregnation process starts, the temperature is kept constant, whereas the pressure changes from ambient pressure to 60 mbar every fifteen minutes.

A complete cycle consists of fifteen minutes at 60 mbar and fifteen minutes at ambient pressure, for this reason the whole process takes up three hours.

At the end of the six cycles, after cooling the solution, we can remove the three impregnated papers from the flask to move them into the oven and let them dry at a temperature of 105°C.

After forty-eight hours in the oven, the specimens are weighed and analysed.

Now we make a list of all impregnation tests in order to report all the values that then will be summarized in a table. During these impregnation tests a parameter has always been changed, for example the type of electrolyte, the temperature or the duration of the process.

Our final goal is to compare the differences implemented in the impregnation process, with the differences in the electrical capacitance of the final device.

6.4.1 - Impregnation n°1

In the first impregnation test that was performed it was used the A55m electrolyte solution simulating the process that takes place in the company at industrial scale: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 85°C.

Paper separator dimension and weight:

Paper a: 4.1 cm x 2.3 cm initial weight: 0.0187 g

Paper b: 3.6 cm x 2.2 cm initial weight: 0.0246 g

Paper c: 4.0 cm x 2.2 cm initial weight: 0.0285 g

Measure of the weight of these samples after the impregnation process and the drying in the oven:

Paper a: final weight: 0.0576 g $\Delta = 0.0389$ g

Paper b: final weight: 0.0970 g $\Delta = 0.0724$ g

Paper c: final weight: 0.1928 g $\Delta = 0.1643$ g

After these measurements, it could be calculated the amount of solute adsorbed in the paper. Impregnation value (g/cm^3):

A55m on paper separator a: 2.0625 g/cm^3

A55m on paper separator b: 2.2853 g/cm^3

A55m on paper separator c: 3.7341 g/cm^3

6.4.2 - Impregnation n°2

In the second impregnation test that was performed it was used the same electrolyte solution but in this case the temperature at which the process is tested is changed: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for three times.

The temperature is fixed at 65°C.

Paper separator dimension and weight:

Paper a: 3.5 cm x 3.5 cm initial weight: 0.0238 g

Paper b: 3.5 cm x 3.5 cm initial weight: 0.0349 g

Paper c: 3.5 cm x 3.5 cm initial weight: 0.0402 g

Measure of the weight the samples after the impregnation process and the drying:

Paper a: final weight: 0.0773 g Δ = 0.0535 g

Paper b: final weight: 0.0777 g Δ = 0.0428 g

Paper c: final weight: 0.0989 g Δ = 0.0587 g

After these measurements it is possible to calculate the amount of solute trapped in the paper. Impregnation value (g/cm^3):

A55m on paper separator a: 2.1836 g/cm^3

A55m on paper separator b: 0.8734 g/cm^3

A55m on paper separator c: 0.9592 g/cm^3

In this test, carried out with lower impregnation temperatures, viscosity plays an important role since the amount of impregnated which remains is lower but the value of paper remains unchanged, probably due to a different position held during the 48 hours of drying in the oven.

6.4.3 - Impregnation n°3

During the third impregnation test, the A55m electrolytic solution was used again. In this case the temperature was kept constant and the parameter change is the reduction of number of cycles which halve the process times: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for three times. The temperature is fixed at 85°C.

Paper separator dimension and weight:

Paper a: 4.0 cm x 4.0 cm initial weight: 0. 0313 g

Paper b: 4.0 cm x 4.0 cm initial weight: 0. 0474 g

Paper c: 4.0 cm x 4.0 cm initial weight: 0. 0563 g

Measure of the weight of the samples after the impregnation process and the drying in the oven gives these values:

Paper a: final weight: 0. 0377g Δ = 0.0064 g

Paper b: final weight: 0. 0611g Δ = 0.0137 g

Paper c: final weight: 0. 0736g Δ = 0.0173 g

After these measurements, we can calculate the amount of solute trapped in the paper calculated.

Impregnation value (g/cm^3):

A55m on paper separator a: 0.2000 g/cm^3

A55m on paper separator b: 0.2141 g/cm^3

A55m on paper separator c: 0.2163 g/cm^3

6.4.4 - Impregnation n°4

During this test the electrolytic solution was changed, in this impregnation test it was used the A55p solution. The impregnation simulates the same process that occurs in the company: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 85°C.

Paper separator dimension and weight:

Paper a: 4.5 cm x 4.2 cm initial weight: 0. 0370 g

Paper b: 4.7 cm x 4.4 cm initial weight: 0.0592 g

Paper c: 4.2 cm x 4.6 cm initial weight: 0.0677 g

The samples weight is measured after the impregnation process and the drying in the oven:

Paper a: final weight: 0. 0604g Δ = 0.0234 g

Paper b: final weight: 0. 1119g Δ = 0.0527 g

Paper c: final weight: 0. 1003g Δ = 0.0326 g

After these measurements, it is possible to calculate the amount of solute remained in the paper.

Impregnation value (g/cm^3):

A55p on paper separator a: 0.6190 g/cm^3

A55p on paper separator b: 0.6372 g/cm^3

A55p on paper separator c: 0.3375 g/cm^3

6.4.5 - Impregnation n°5

During this test A55p solution is used: there is a change in the temperature at which the process was tested: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 65°C

Paper separator dimension and weight:

Paper a: 3.5 cm x 3.5 cm	initial weight: 0.0211 g
Paper b: 3.5 cm x 3.5 cm	initial weight: 0.0388 g
Paper c: 3.5 cm x 3.5 cm	initial weight: 0.0397 g

Measure of the weight the samples after the impregnation process and the drying in the oven:

Paper a: final weight: 0.0233 g	Δ = 0.0022 g
Paper b: final weight: 0.374 g	Δ = 0.0036 g
Paper c: final weight: 0.0397 g	Δ = 0.0066 g

After these measurements, it is possible to calculate the amount of solute trapped in the paper.

Impregnation value (g/cm^3):

A55p on paper separator a: 0.0883 g/cm^3

A55p on paper separator b: 0.0735 g/cm^3

A55p on paper separator c: 0.1077 g/cm^3

6.4.6 - Impregnation n°6

During the third impregnation test the A55p electrolytic solution was yet used. In this case the temperature was kept constant and the parameter change is the reduction of number of cycles that halve the process times: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for three times. The temperature is fixed at 85°C.

Paper separator dimension and weight:

Paper a: 4.0 cm x 4.0 cm initial weight: 0.0312 g

Paper b: 4.0 cm x 4.0 cm initial weight: 0. 0472 g

Paper c: 4.0 cm x 4.0 cm initial weight: 0. 0522 g

The measurement of the weight of the samples is taken after the impregnation process and the drying in the oven:

Paper a: final weight: 0.0420 g $\Delta = 0.0108$ g

Paper b: final weight: 0.0612 g $\Delta = 0.0140$ g

Paper c: final weight: 0.0677 g $\Delta = 0.0155$ g

After these measurements, it is possible to calculate the amount of solute adsorbed in the paper.

Impregnation value (g/cm^3):

A55p on paper separator a: 0.3375 g/cm^3

A55p on paper separator b: 0.2187 g/cm^3

A55p on paper separator c: 0.1937 g/cm^3

6.4.7 - Impregnation n°7

In this impregnation, we tested the last electrolyte solution, the H2000 solution.

In this case we utilized the standard condition: fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times.

The temperature is fixed at 85°C.

Paper separator dimension and weight:

Paper a: 4.1 cm x 1.9 cm initial weight: 0.0155 g

Paper b: 4.3 cm x 1.9 cm initial weight: 0. 0218 g

Paper c: 4.4 cm x 2.0 cm initial weight: 0. 0316 g

Measure of the weight the samples after the impregnation process and the drying in the oven:

Paper a: final weight: 0.0315 g Δ = 0.0160 g

Paper b: final weight: 0.0404 g Δ = 0.0222 g

Paper c: final weight: 0.0669 g Δ = 0.0353 g

After these measurements, we can calculate the amount of solute trapped in the paper.

Impregnation value (g/cm^3):

A55p on paper separator a: 1.0256 g/cm^3

A55p on paper separator b: 0.6793 g/cm^3

A55p on paper separator c: 0.8023 g/cm^3

In the following table the impregnation values of all the tests carried out are shown in order to clarify the trends of the measured weight with respect to the change in parameters impregnation process:

Tab. n°1

Electrolytic solution	Paper separator	Temperature (°C)	Number of cycles	Impregnation in g/cm³
A55m	Kraft a	85	Six	2.0625
A55m	Kraft b	85	Six	2.2853
A55m	Kraft c	85	Six	3.7341
A55m	Kraft a	65	Six	2.1836
A55m	Kraft b	65	Six	0.8734
A55m	Kraft c	65	Six	0.9592
A55m	Kraft a	85	Three	0.2000
A55m	Kraft b	85	Three	0.2141
A55m	Kraft c	85	Three	0.2163
A55p	Kraft a	85	Six	0.6190
A55p	Kraft b	85	Six	0.6372
A55p	Kraft c	85	Six	0.3375
A55p	Kraft a	65	Six	0.0883
A55p	Kraft b	65	Six	0.0735
A55p	Kraft c	65	Six	0.1077
A55p	Kraft a	85	Three	0.3375
A55p	Kraft b	85	Three	0.2187
A55p	Kraft c	85	Three	0.1937
H2000	Kraft a	85	Six	1.0256
H2000	Kraft b	85	Six	0.6793
H2000	Kraft c	85	Six	0.8023

From this table it is immediately clear that the most suitable situation for impregnation takes place at the highest temperature and with the longest process with the highest possible number of cycles.

Among these tests, it can be seen that the best impregnating liquid electrolyte is the most viscous, this is probably due to the fact that, being more viscous, this solution remains trapped with more solute content during drying.

Regarding the difference in weight with respect to the separating paper used it must be said that this difference depends largely on the initial volume of the paper, the tests carried out on the thinner and more dense paper have provided lower impregnation values because there is less paper porosity exploitable by the solution.

In the other two samples, the composition of the paper is very similar, therefore the difference lies in the fact that the paper separator c is thicker and therefore has a larger volume to be soaked with the electrolyte solution.

By changing the initial parameters, a sharp decrease in the impregnation values is noted: regarding the first solution used (A55m) it can be observed that the temperature reduction causes a decrease in the quantity of impregnated electrolyte solution.

The drop in temperature reduces to one third the quantity of impregnated electrolyte, except in one case: when the impregnate paper is the rigid one. In that case a small part of dried electrolyte remains on the paper surface, in addition to electrolyte inside the volume of paper. This solute present on samples surface is due to a wrong position during the drying process.

By reducing the number of cycles, the decrease is even more evident: in this case the quantity of electrolyte left in the volume of the separating paper is about one tenth.

As regards the second electrolyte solution, as mentioned above, the impregnation value with respect to the A55m solution is lower.

In the case of tests performed with reduce temperature or time, the expectation is to obtain lower impregnation values. In the case of use of A55p the trend is reversed.

A decrease in temperature of 20°C causes a drop in the weight of electrolyte impregnated by a tenth of the initial value, while a decrease in the duration, through the halving of the number of cycles brings the value of electrolyte solution impregnated to about one half or one third of the value obtained with the standard process.

As for the third solution (H2000) we have only carried out the impregnation with the standard parameters: from this test it results that the solution with the lower viscosity impregnates more the paper with the lower density.

The impregnation performed by immersion in that electrolyte shows intermediate values between the two solutions tested first.

This kind of information is quantitative information therefore could not provide us information about the type of solute that remains impregnated in the cellulose of the paper, but could give us an idea of which impregnation process parameters are more effective.

6.5 - Impregnation of Aluminium

After the paper separator impregnation, let's pay attention to impregnation of the aluminium foils.

There are two different aluminium foils:

- The oxidized foil that is the anode (the heaviest and most opaque lamina)
- The thinner foil that forms the cathode.

We start with the anode foils:

Anode foil: 2.8 cm x 3.2 cm

The weight before the impregnation is w = 0.2420 g

The weight after the impregnation process depends on the temperature at which it is performed the process:

- With the temperature fixed at 65 °C the final weight is: 0.2466 g
- With the temperature fixed at 85 °C the final weight is: 0.2599 g

Cathode foil: 2.8 cm x 3.2 cm

The weight before the impregnation is w= 0.0410 g

The weight after the impregnation process depends on the temperature at which we perform the process:

- With the temperature fixed at 65 °C the final weight is: 0.0544 g
- With the temperature fixed at 85 °C the final weight is: 0.0747 g

Tab n°2

Electrolytic solution	Aluminium foil	Temperature (°C)	Δ Weight (g)
A55m	Anode	85	0.0179
A55m	Anode	65	0.0046
A55m	Cathode	85	0.0337
A55m	Cathode	65	0.0134

This result is unexpected, because the surface of the anode, increased by the etching process, should be able to absorb more electrolyte solution due to the larger surface, instead from the experimental data it results the opposite.

We can explain this unexpected measure in two ways:

- On the cathode there is not the oxide layer, present on the anode (due to forming process), for this reason, during the immersion of the foil in the high temperature electrolyte solution, a re-hydration of the aluminium could occur. This could be a mechanism to explain the high increment in weight of the cathode foil.
- The drying position in the furnace may have influenced the final measurement of the weights as a small amount of electrolyte remained deposited on the edge of the aluminium sample.

In any case, the reduction in temperature leads to results similar to those found with the impregnation of paper samples: a reduction of about twenty degrees in temperature causes a reduction in weight of impregnated electrolyte.

6.6 - Impregnation of capacitor

This is the last impregnation test carried out in laboratory: this test includes all the materials treated up to now as it is the impregnation of an already wrapped condenser, comprising the two aluminium foils (anode and cathode) and two layers of separating paper between them.

The 20 µm rigid paper is placed on the side of the cathode while the soft 50 µm paper is placed in contact with the oxide formed on the anode.

In this way more wettability is provided on the surface of the anode: the oxide layer can exploit the higher specific surface and the soft paper composition to achieve the best wettability possible.

When the process starts, the capacitor is completely immersed in the electrolyte solution, after which the impregnation process is carried out in four different ways:

- Test 1: impregnation carried out with A55m electrolytic solution, the process is performed with fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 85°C.

initial weight of wrapped capacitor: 14.626 g

final weight after impregnation process: 16.092 g

- Test 2: impregnation carried out with A55m electrolytic solution, the process is performed with fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 65°C.

initial weight of wrapped capacitor: 14.617 g

final weight after impregnation process: 15.323 g

- Test 3: impregnation carried out with A55p electrolytic solution, the process is performed with fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 85°C.

initial weight of wrapped capacitor: 14.591 g

final weight after impregnation process: 15.599 g

- Test 4: impregnation carried out with A55m electrolytic solution, the process is performed with fifteen minute cycles at 60 mbar and fifteen minute cycles at room pressure, repeated for six times. The temperature is fixed at 65°C.

initial weight of wrapped capacitor: 14.515 g

final weight after impregnation process: 15.069 g

Tab. n°3

Electrolytic solution	Temperature (°C)	Δ Weight (g)	Impregnated weight in %
A55m	85	1.465	10.02
A55m	65	0.706	4.83
A55p	85	1.007	6.90
A55p	65	0.554	3.82

Looking at the table it must be said that the trend observed until now following the change in temperature is confirmed with the impregnation of the already wrapped condensers. The most viscous solution impregnates greater amounts of solute than the second solution and a reduction of 20°C in temperature halves the amount of electrolyte left in the separator paper.

6.7 - Characterization of impregnated samples

The samples have been analysed after forty eight hours in the oven, in order to reduce as much as possible the water content in the paper separator sample.

The weight measurements confirm that the paper samples were impregnated with the electrolyte solution, since there is still a difference in weight.

Through thermogravimetric analysis we can compare the difference between virgin paper before impregnation (20 µm thickness rigid paper) and the same paper separator after having carried out impregnation for each different electrolyte solutions.

6.7.1 - Thermogravimetric analysis of impregnated samples

TG of rigid paper separator, impregnated with A55m under standard condition:

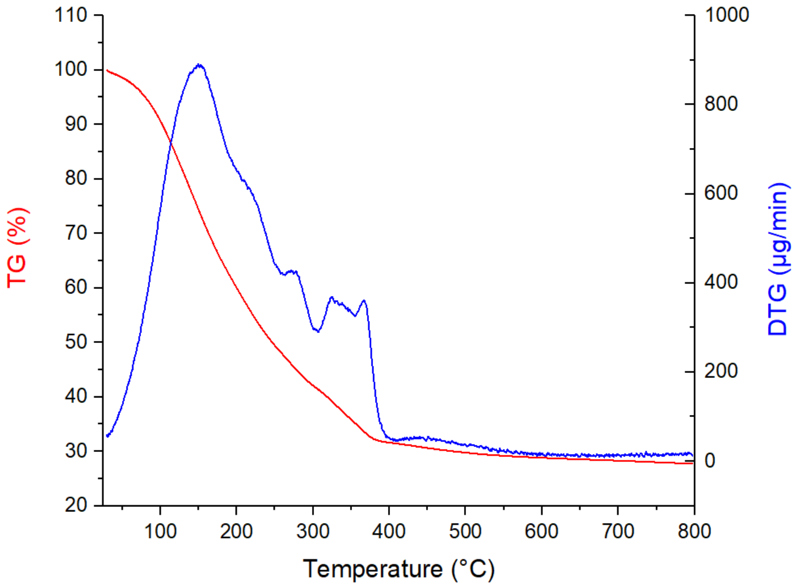

Fig. n°30: TG of rigid paper, after impregnation in A55m solution

TG of rigid paper separator, impregnated with A55p under standard condition:

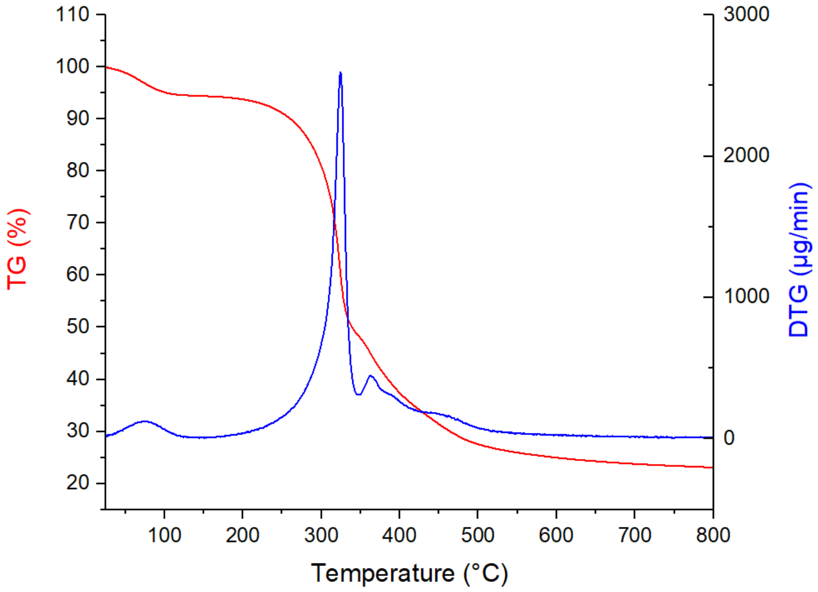

Fig. n°31: TG of rigid paper, after impregnation in A55p solution

TG of rigid paper separator, impregnated with H2000 solution under standard condition:

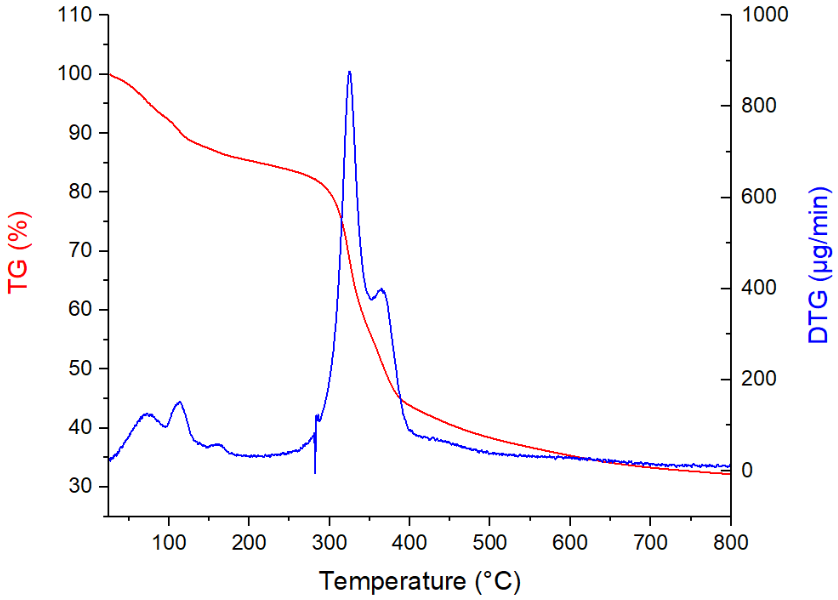

Fig. n°32: TG of rigid paper, after impregnation in H2000 solution

Comparing the graphs, it is possible to note the displacement to the left of the peak of the DTG curve when thermogravimetric test is carried out on impregnated samples.

The DTG graph of virgin paper sample has a sharp peak around 350°C, while the other thermogravimetric graphs, come from test carried out on impregnated paper separator samples, shown a left-shift of the sharp peak compared to the graphs obtained from the test carried out on the virgin paper separator samples. Moreover, this peak is no longer as narrow as in the first case, virgin paper analysis, or in the case of H2000 solution analysis, but is wider.

In the virgin paper separator the weight loss occurs abruptly in a range of temperature between 300°C and 360°C, in this temperature range the cellulose lost almost all of its weight.

In H2000 electrolytic solution the sharp loss in weight occurs above 400°C.

The left-shift of the peak and the width of the band can be traced back to the impregnation due to the higher difference compound presence.

Especially in the case of the sample impregnated with the more viscous solution (A55m), the range of the weight loss of the specimen is much larger, this is due to the greater amount of components present in the volume of paper analysed.

At 100°C there is a loss in weight due to the evaporation of water, the organic compounds such as mono-ethylene glycol lost weight around 200°C, at the end the cellulose burn between 300°C and 400°C (as shown the TG of virgin paper separator).

Another difference that it’s possible to appreciate from the comparison between the graphs obtained by the thermogravimetric analysis on the paper separator sample, before and after the impregnation process, is that at the end of the test (800°C) there is a difference in weight percentage, meaning that different residues have been obtained.

In the first case the sample of virgin paper retains less than 20% of its initial weight.

In the case of the impregnated sample, at the end of the test, it is about 30% of the weight of the specimen before the analysis. The excess percentage is related to the amount of compounds (like salts) trapped in the volume of paper, largely composed of borates.

Regarding the thermogravimetric tests of the other two impregnated samples (one impregnated in A55p and the other impregnated in H2000 electrolytic solution) the left-shift is less pronounced and the amplitude of the peaks is less wide than in the first case.

There is a slight reduction in weight around 100°C, due to the loss of water and a sharp reduction of the weight between 300°C and 350°C due to paper separator evaporation.

After the end of the test (once reached 800°C) there is the possibility of checking the percentage weight reported and estimate what kind of electrolytic solution remains more than others in the volume of paper separator. The sample that at the end of the test has the highest value of remained weight is the one impregnated with the H2000 solution (about 35% of initial weight).

6.7.2 - IR spectrometry analysis of impregnated samples

Through the comparison of graphs obtained from the analysis of samples impregnated with the electrolytes and the IR spectra of virgin rigid paper separator is possible to observe the different behaviour of samples, impregnated in different way.

It has to be said that the sample of non-impregnated paper, shown in Fig n°20, reflects the composition of the pure cellulose: peak in cellulose’s IR spectroscopy graph are due to O-H vibration at frequency about 3000 cm^{-1}, other significant peaks comes at lower wavenumber (under 1500 cm^{-1}) from the CH-OH, C-O, C-OH and C-Cl vibration.

Starting from the IR graph of the virgin paper, is difficult to explain the change due to the impregnation shown in the figure due to the high content of different compounds (cellulose, little amount of water, glycols, borate salts).

It is possible to note that in IR graphics of impregnated sample new peaks are present due to solute content. These peaks can be at high wavenumber (>3000 cm^{-1}) due to water remained in the sample and mostly due to glycol functional group (OH), at lower wavenumber is possible note the peaks of borate vibration, that occur at lower wavenumber (about 1000-1100 cm^{-1})

Regarding the IR spectra of the impregnated specimens, there is the possibility to find some information about the electrolytic solution composition and about the impregnation process comparing each other.

Starting from the plot of IR analysis carried out on specimen impregnated with A55m at different temperature it must be said that the spectrum shape is similar, but in the case of the sample obtained with a impregnation performed at 85°C more solute remains impregnated and for this reason the value of transmittance is higher.

Moreover the samples impregnated in standard condition (at 85°C) show a higher presence of O-H vibration at higher frequency (>3000 cm^{-1}) with respect to the sample impregnated at lower temperature.

These O-H vibrations are due to water and mostly to glycols content; the difference between two impregnated paper specimens comes from that in the first case the impregnation is more effective and for this reason the solute content in paper separator is higher.

It has to be said that in all case the graph of sample impregnated in standard condition with the more viscous solution (A55m) is the one that shows the higher value of transmittance and is the one in which the water and glycol presence is more marked.

The recognition of other characteristic peaks is made difficult by the high number of chemical compounds inside the sample.

All these chemical compounds could slightly change the shape and the position of a vibrational peak.

IR spectroscopy of rigid paper, impregnated with A55m maintain standard condition:

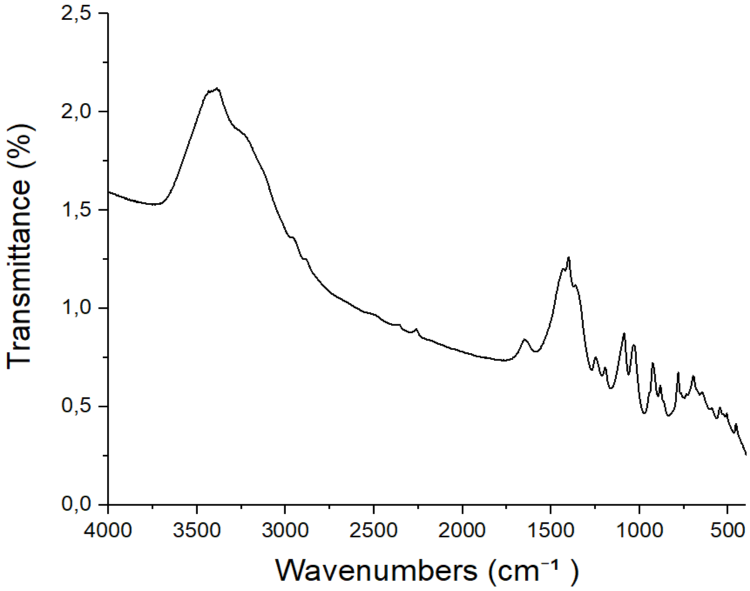

Fig. n°33: Spectrum of rigid paper sample, impregnated in A55m solution (at 85°C)

IR spectroscopy of rigid paper separator, impregnated with A55m at 65°C.

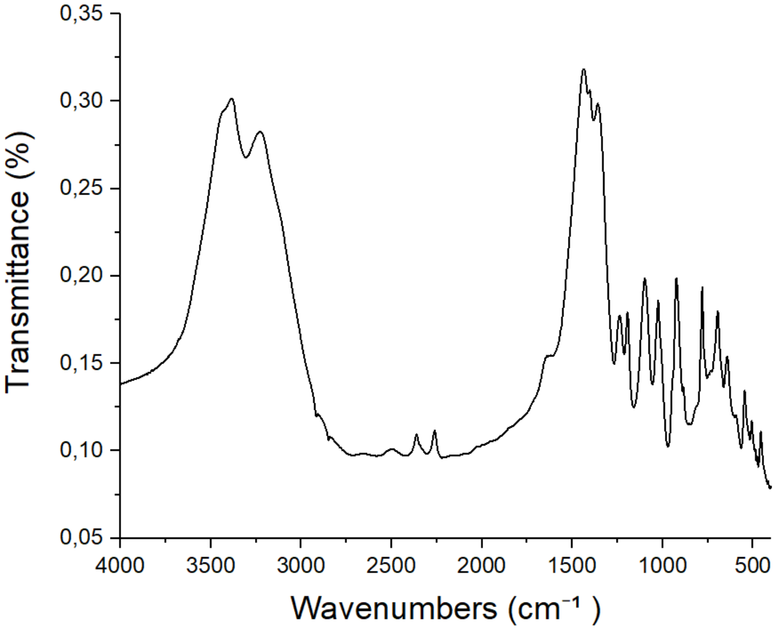

Fig. n°34: Spectrum of rigid paper sample, impregnated in A55m solution (at 65°C)

IR spectroscopy of rigid paper, impregnated with A55p maintain standard condition:

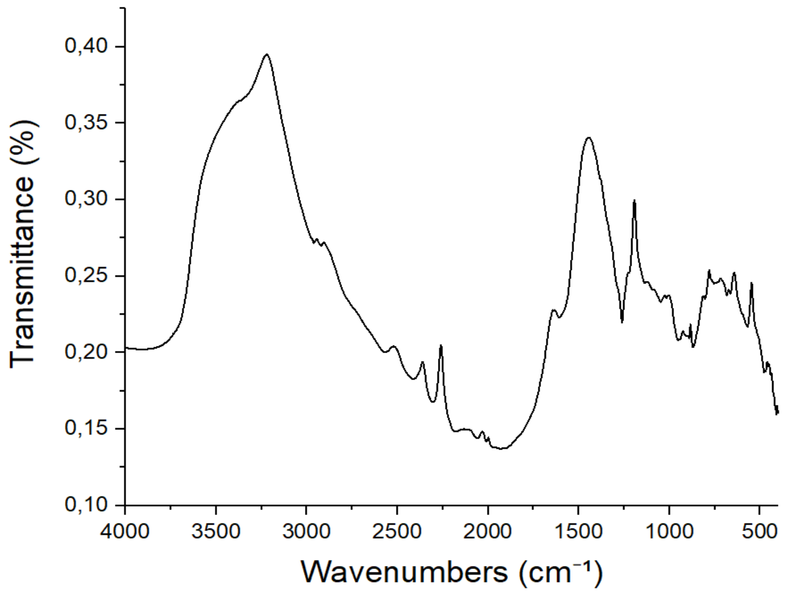

Fig. n°35: Spectrum of rigid paper sample, impregnated in A55p solution (at 85°C)

IR spectroscopy of rigid paper, impregnated with H2000 under standard condition:

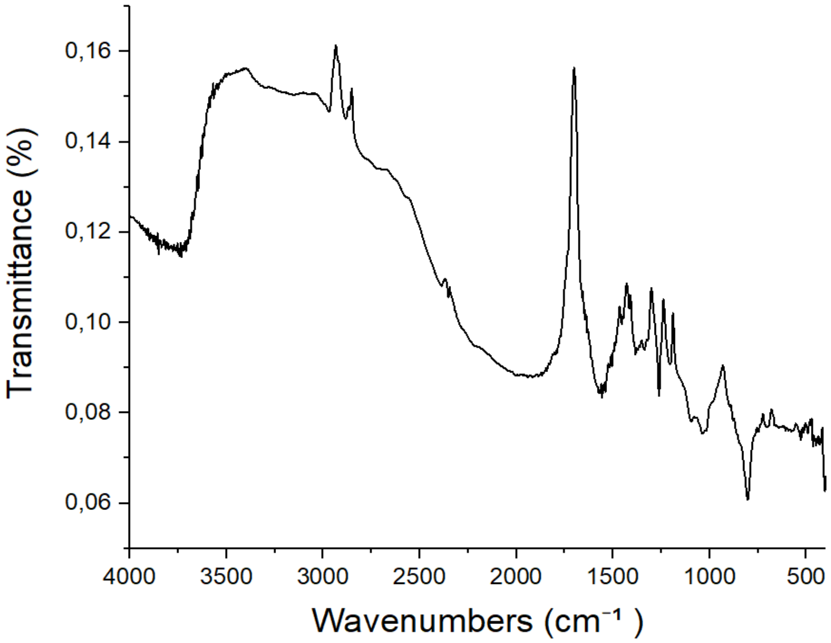

Fig. n°36: Spectrum of rigid paper sample, impregnated in H2000 solution (at 85°C)

6.7.3 – Charge test on capacitors

In order to carry out these characterization tests, two identical capacitors impregnated under different conditions are used:

- The capacitors tested are impregnated with the more viscous solution (A55m electrolytic solution).
- The capacitors tested are impregnated at first at a temperature of 85°C (standard process), and then at 65°C.

These tests are performed in order to compare the differences in weight and the difference in value capacitance measured on the capacitors impregnated at the two different temperature. Charge test is performed first on the capacitor impregnated at 85°C and test are carried out at different current and up to 380 V. With this test is possible to measure the value of capacitance and other electrical parameters (as Rs and Rp).

Because the series resistance is consistently high, through this measurement the only electrical property that it is possible to estimate with certain value is the capacitance.

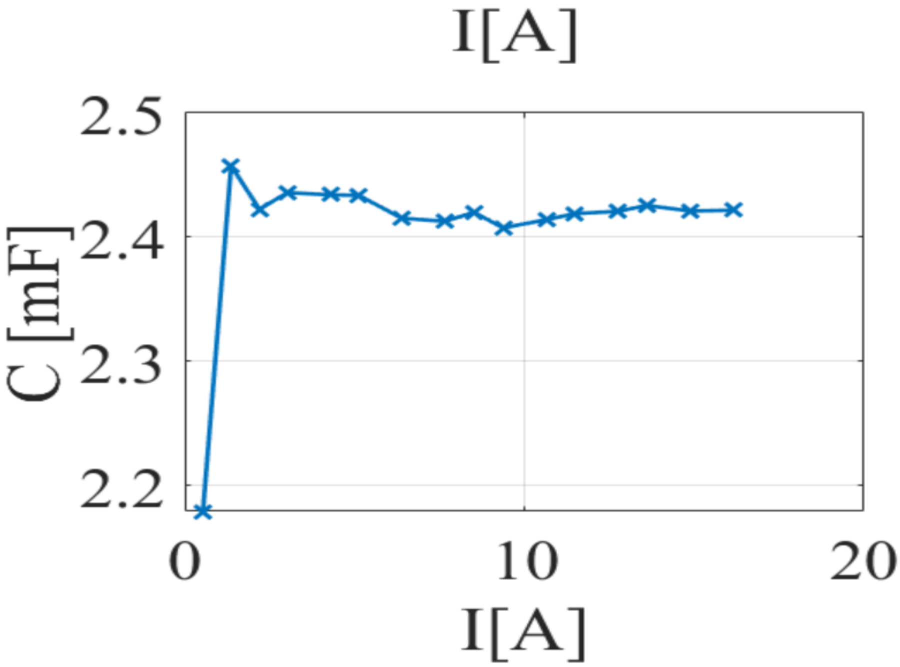

Fig. n°37: Capacitance of capacitors immersed in A55m at 85°C

From the test we it is possible to note that the capacitance value is settled at 2.4 mF, that is obtained at medium-high current value.

The second charge test is performed on a capacitor that was obtained after impregnation with A55m at 65°C.

This measurement of capacitance was directly plotted in a graph compared to the value of capacitance obtained in the first case.

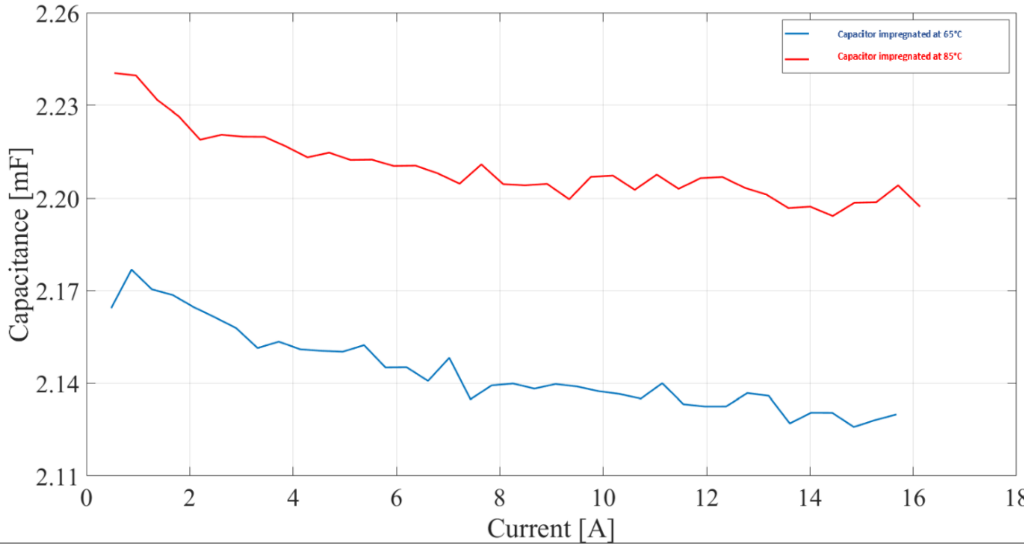

Fig. n°38: Capacitance of capacitors obtained with different process parameters

Comparing the graphs, it is possible to note that the capacitor obtained with the process performed at lower temperature was characterized by lower capacitance value.

The two curve in the plot seems to have similar behaviour, at low current have lower capacitance values, after reaching medium-high current the two curves stabilize.

CHAPTER 7

7.1 – Conclusions

The aim of this research was to study in detail the impregnation process that is carried out during the production phase of an aluminium electrolytic capacitor.

Although the discovery of this type of condenser goes back in time and that in the past years other capacitors have been developed with higher capacitance values, the aluminium electrolytic capacitors still obtain great success thanks to their versatility and the low production cost.

Their production process is still studied today, particularly because of their importance and success in the market worldwide.

Specifically, the objective of this research was to study the reduction of production costs by intervening on the impregnation process that occurs during production.

By comparing the samples obtained through the impregnation performed with different operating parameters, it has been assumed that the most effective process, in terms of the weight of the solution remained impregnated, is the most expensive one.

This is the impregnation process that is done in the factory under standard conditions: the impregnation takes place at a temperature of 85°C, for 6 cycles.

Each cycle consists of two phases: fifteen minutes at a pressure of 0.6 mbar and fifteen minutes at room pressure.

The results obtained by performing this impregnation process with the three electrolytic solutions (used in the company for the construction of capacitors) reveal that the solution that shows the greatest effectiveness in terms of impregnation, is the most viscous one, the A55m solution.

To verify the possibility of reduction of production costs related to the impregnation process, it was decided to proceed with the impregnation phase with two different approaches, intervening on the temperature and the duration of the process.

In the first case, the temperature process has been reduced by twenty degrees, whereas in the second case the number of cycles was reduced in order to make the duration process last half of the time that it was before.

The analysis of the results obtained shows that in most cases these two changes in the standard parameters drastically reduced the effectiveness of the impregnation process.

Non-optimal impregnation is a problem because the electrolyte will not be able to correctly connect the cathode surface with the dielectric surface, generating current losses.

In some cases, by reducing the process temperature, the usual and clear reduction in the weight of the electrolyte that remained impregnated in the paper, was not observed.

This deviation from the trend is observed, for example, in the specimen of rigid paper separator impregnated at 65°C with the solution A55m.

The deviation in impregnation value probably is due to the different position maintained in the oven, this caused the electrolyte solution to settle above the surface of the paper during drying.

The dried electrolytic solution above the paper separator sample is a problem because it is enough to invalidate the value of the electrolyte weight impregnated within the paper volume.

In any case, the reproducibility of the results obtained by experimenting with the process at reduced temperature was much more encouraging than the results achieved by reducing the number of impregnation cycles.

By lowering the temperature, it could be seen that in most cases the delta in weight was halved, meaning that about half of the solute remained impregnated, compared to the standard process.

Therefore it is decided to proceed with the immersion of two capacitors, already wrapped, ready to be impregnated and sealed.

These capacitors were impregnated with two solutions, the A55m and the A55p solution. The only difference between them is the amount of water and therefore the viscosity.

As mentioned previously, the condenser impregnated at a higher temperature and with the highest number of cycles, was the one with the highest amount of impregnated solute.

Furthermore, it was verified that the trend, due to the temperature reduction, was respected. Indeed using both solutions, the test at 65°C reveals delta by half weight.

For this reason, the charge tests have been done in order to effectively test the quality of the products obtained through the process made at reduced temperatures.

The two capacitors immersed in the most viscous solution were chosen as samples of the charge test.

In the case of the capacitor impregnated with the standard process, the results showed a steady-state capacitance of 2.4 mF, which is very close to the capacity estimated in the company.

In the case of the capacitor impregnated with the process performed at lower temperature, the results showed a lower steady-state capacitance value, about 2.2 mF.

As it can be seen, the reduction in efficiency in terms of capacitance, following impregnation at 65°C, does not affect sharply the overall capacitor performance.

Indeed, that value is comparable with the one found in the experimentation under standard conditions typical of the industrial process.

This result therefore presents great potential, being the first positive premise to the feasibility of a future development of a low temperature impregnation process with energy and cost savings.

References

[1] Meltzer, David E., and Valerie K. Otero. "A brief history of physics education in the United States." American Journal of Physics 83.5 (2015): 447-458.

[2] Sarjeant, W. "Capacitors." IEEE Transactions on Electrical Insulation 25.5 (1990): 861-922.

[3] F. Lionetti, Elaborato di laurea. Electrochemical etching of Aluminium foils for capacitors, 2007-2008.

[4] Bird, John. Electrical and electronic principles and technology. Routledge, 2010.

[5] Ulaby, Fawwaz T., Eric Michielssen, and Umberto Ravaioli. Fundamentals of Applied Electromagnetics 6e. Prentice Hall, 2001.

[6] Both, Jens. "The modern era of aluminum electrolytic capacitors." IEEE Electrical Insulation Magazine 31.4 (2015): 24-34.

[7] Williams, Henry Smith. A History of Science Volume II, The Leyden Jar Discovered, 2013.

[8] Kahn, Louis. "Capacitors-1959." IRE Transactions on Component Parts 6.3 (1959): 150-174.

[9] Keithley, Joseph F. The Story of Electrical and Magnetic Measurements, 2013.

[10] Charles Pollack. D.R.P. 92564, granted 19. May 1897.

[11] Both, Jens. "Electrolytic capacitors, 1890 to 1925: early history and basic principle." IEEE Electrical Insulation Magazine 31.1 (2015): 22-29.

[12] Ho, Janet, T. Richard Jow, and Steven Boggs. "Historical introduction to capacitor technology." IEEE Electrical Insulation Magazine 26.1 (2010).

[13] O'phelan, Michael J., et al. "Electrolytic capacitor and multi-anodic attachment." U.S. Patent No. 6,597,564. 22 Jul. 2003.

[14] A. Albertsen, Jianghai Europe. "Keep your distance – Voltage Proof of Electrolytic Capacitors", 2013.

[15] Niwa, Shinichi, and Yutaka Taketani. "Development of new series of aluminium solid capacitors with organic semiconductive electrolyte (OS-CON)." Journal of power sources 60.2 (1996): 165-171.

[16] Nichcon Corporation. General Descriptions of Aluminum Electrolytic Capacitors, Technical notes. Cat.8101-E.

[17] Rubycon corporation. “technical notes for electrolytic capacitor”

[18] Panasonic. Production of Aluminum Electrolytic Capacitors, 2014.

[19] CapXon. Manufacturing Process, 2015

[20] Osawa, N., and K. Fukuoka. "Pit nucleation behavior of aluminium foil for electrolytic capacitors during early stage of DC etching." Corrosion science 42.3 (2000): 585-597.

[21] Zhu, S. Q., et al. "Modelling specific capacitance of DC etched aluminium foil for aluminium electrolytic capacitor." Journal of Materials Science: Materials in Electronics 26.9 (2015): 6750-6756.

[22] Borsody, Lorant. "New Impregnation for Paper Capacitors." IRE Transactions on Component Parts 7.1 (1960): 15-25.

[23] Parler, Sam G. "Improved spice models of aluminum electrolytic capacitors for inverter applications." Industry Applications Conference, 2002. 37th IAS Annual Meeting. Conference Record of the. Vol. 4. IEEE, 2002.

[24] Peekema, R. M., and J. P. Beesley. "Factors affecting the impedance of foil-type electrolytic capacitors." ELECTROCHEM TECHNOL 6.5 (1968): 166-172.

[25Berduque, Alfonso, et al. "Low ESR aluminium electrolytic capacitors for medium to high voltage applications." CARTS USA, 2011 Proc.. 2011.

[26] Khandebharad, R., R. B. Dhumale, and S. S. Lokhande. "Online Failure Prediction of the Aluminum Electrolytic Capacitor." Int. J. Science and Research 4.6 (2015): 2099-2102.

[27] Simon, Isolde, et al. "Micromachined metal oxide gas sensors: opportunities to improve sensor performance." Sensors and Actuators B: Chemical 73.1 (2001): 1-26

[28] Parler, Sam, and Cornell Dubilier. "1Heating in Aluminum Electrolytic Strobe and Photoflash Capacitors by." (2007).

[29] J.L. Stevens, A.C. Geiculescu, T.F. Strange. Dielectric Aluminum Oxides: Nano-Structural Features and Composites, 2014.

[30] Strange, Thomas F., and Timothy R. Marshall. "Very high volt oxide formation of aluminum for electrolytic capacitors." U.S. Patent No. 6,299,752. 9 Oct. 2001.

[31] Chang, Jeng-Kuei, et al. "Effect of heat-treatment on characteristics of anodized aluminum oxide formed in ammonium adipate solution." Journal of the Electrochemical Society 151.3 (2004): B188-B194.

[32] Thiesbürger, K. H. Der Elektrolyt-Kondensator. Roederstein, 1991.

[33] Dombro, Ronald A. "Electrolyte for high voltage electrolytic capacitors and methods." U.S. Patent No. 8,734,667. 27 May 2014.

[34] Kolosnitsyn, Vladimir, and Elena Karaseva. "Battery electrode structure and method for manufacture thereof." U.S. Patent Application No. 11/190,203.

[35] Berduque, Alfonso, Zongli Dou, and Rong Xu. "Electrochemical Studies for Aluminium Electrolytic Capacitor Applications: Corrosion Analysis of Aluminium in Ethylene Glycol-Based Electrolytes." CARTS-Europe Virtual Conference. 2009.

[36] http://www.itelcond.it/en/home-3/

[37] Sillars, Fiona B., et al. "Variation of electrochemical capacitor performance with room temperature ionic liquid electrolyte viscosity and ion size." Physical Chemistry Chemical Physics14.17 (2012): 6094-6100.

[38] V. Librando, Z. Minniti, S. Lorusso. “Ancient and modern paper characterization”, Unibo.