CAPACITORS AND CONDUCTING POLYMERS: DEVELOPMENT OF CONDUCTING POLYMER, INGREDIENTS AND THEIR CHEMISTRY

A Major – II Project Report submitted for the partial fulfillment of the award for the degree of

MASTER OF TECHNOLOGY

IN

POLYMER TECHNOLOGY

Submitted by

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DECLARATION

I**,** Rishi Gupta**,** hereby declare that the thesis entitled **“Capacitors and conducting polymers: Development of conducting polymer, ingredients and their chemistry”** is an authentic record of research work done by me under the supervision of Dr. Richa Srivastava, **Assistant professor,** Delhi Technological University**.** It has not been copied from any source without giving its proper reference, except where due acknowledgement has been made in the text. This work has not been previously submitted for the award of any degree or diploma of this or any other University Institute.

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CERTIFICATE

This is to certify that the project report entitled **“Capacitors and conducting polymers: Development of conducting polymer, ingredients and their chemistry”** submitted by Rishi Gupta (Roll No. 2K14/PTE/07) in partial fulfillment for the award of degree of Masters of Technology in Polymer Technology to Delhi Technological University, Delhi – 110042, is the students own work carried out by him under my supervision. The project embodies the original work done by him to the best of our knowledge and has not been submitted to any other degree of this or any other university. The matter embodied in this project report is original and not copied from any source without proper citation.

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CONTENTS

INTRODUCTION

Together with rapid progress achieved by the electronics industries, electrolytic capacitors for electronic circuits have been miniaturized and are now being manufactured by automated production facilities. Also demand for them is being diversified.

Various organic ammonium compounds are used to meet these production trends for electrolytic capacitors and to replace conventional conducting polymer. To improve the performance of polymer electrolytes, it is necessary to improve their electrical conductivity, boiling points, setting point, viscosity and their anode and cathode corrosion inhibition characteristics.

Basically capacitor is a device which can able to store the charge when potential is applied and able to provide energy whenever require in circuit. There are various kind of capacitors such as mica, ceramic, paper, gold, tantalum capacitor in which conducting polymer play vital role. Aluminum electrolytic capacitors are more popular than others due to wide range of capacitance i.e from 0.1 micro Farad to 3,30,000 micro Farad in 6.3Wv to 451Wv design is possible with longer life in low cost.

Capacitor are normally used to filter the current and commonly used in Television, Radio, Switching power supplies, Computer and in photoflash applications in cameras.

Electrolytic capacitors and its fundamentals

Aluminum Electrolytic Capacitor :

Capacitance : It is the ability of the dielectric to store the charge. Its unit is farad.

Capacitor : It is a device which is having the ability to store electrostatic energy and release such energy under design control conditions .

Type of capacitors:

Dielectric	Construction	Capacitance	Voltage Rating
Air	Meshed plates	10-400 pf	400 V
Ceramic	Tabular disk	0.5 to 1600 pf 0.002 to 0.1 μf	500 to 20,000 V
Electrolytic	Aluminum	0.1 μf to 1Farad	5 to 450 V
	Tantalum	0.1 to 1000 μf	8 to 100 V
Mica	Stacked sheets	10 to 5000 pf	500 to 20000 V
Paper	Rolled foil	0.001 to 1 μf	200 to 1650 V

Advantage electrolytic capacitor

a) High volumetric efficiency i.e. high capacitance per unit volume.
b) Excellent price to performance ratio.

Operation of Electrolytic capacitors: General capacitor can, in theory, use any kind of materials for electrode (anode and cathode) as long as it is a conductor and the same is true for the dielectric as long as it is a good insulator. In addition any of the electrodes can serve as the anode and cathode or vice versa without any problem. However , this is not true with electrolytic capacitor in which anode is limited to value metal only , which form a fine , higher insulative oxide film on its surface during anodic oxidation in an electrolytic solution .

Valve metal

Metals the oxides of which are capable of blocking the current flow in one direction and of passing it in the other are called valve metal. Some of the value metal and there oxide are :

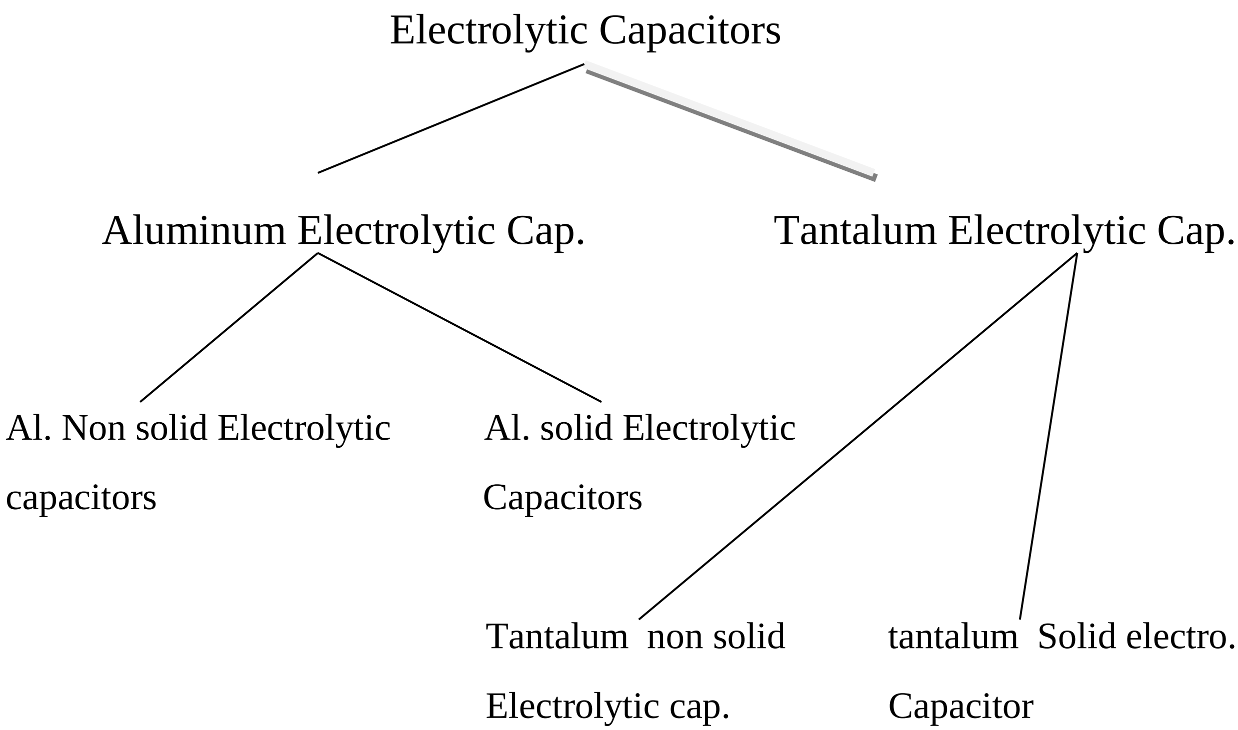
Aluminum (Al.)	Aluminum oxide (Al_2O_3)
Niobium (Nb)	Niobium pent oxide (Nb_2O_5)
Tantalum (Ta)	Tantalum pent oxide (Ta_2O_5)
Titanium (Ti)	Titanium dioxide (TiO_2)
Zirconium (Zr)	Zirconium dioxide (ZrO_2)
Hafnium (Hf)	Hafnium dioxide (HfO_2)

Currently, the only two metal in practical application are Aluminum and tantalum.

The oxide film, that is formed the value metal become as electrical insulator and the function as the dielectric only when the electrodes on which it from is the anode. Therefore, Electrolytic capacitor are in principle, capacitors with polarity.

The cathode of the electrolytic capacitor is form by the liquid or solid electrolyte which is conductive in nature.

Types of Electrolytic Capacitors



FEATURES AND DIFFERENCES

	Aluminum Electrolytic capacitor	**Tantalum Electrolytic Capacitors**
Anode	Aluminum foil : Plain & etched	Sintered body & tantalum powder
Cathode	Semi conducting liquid electrolyte stored in tissue papers	Semi conducting solid electrolyte (MnO_2-magnese dioxide) applied On the anodic oxide foil.
Dielectric	Aluminum oxide (Al_2O_3) generated in electrochemical process by oxidation on anode.	Tantalum pent oxide (Ta_2O_5) Generated in electrochemical process by oxidation on anode.
Voltage range	2V to 500 V	2V to 50 V
Capacitance range	0.1 μf to 1000 mf high capacitance product can be made	0.046 μf to 471 μf High capacitance product are difficult to make

Miniaturization	Advantage in high capacitance range	Advantageous in low capacitance range
Leakage current	Relatively large	Relatively small
Tan $	High	low
Temperature characteristics	Not very good	Good
Frequency characteristics	Not very good	Good
Life	Limited	Semi permanent
Failure	Wear Failure, open	Random failure, increase in L.C short circuit.
Ripple resistance	Can take large ripple current	Can't take large ripple current
Reverse voltage resistance	Relatively strong	Weak
Charge and discharge resistance	Relatively well to sudden charge and discharge	Best to avoid sudden charge and discharge
Solvent resist.	Weak	Strong
Price	Relatively Cheap	Costly
Contacting of cathode	Aluminum foil that covers complete formed anode with a separating tissue paper.	Graphite and conductive silver foil that is applied on the semi conducting coating and soldered To the case or the terminals.

The biggest difference between aluminum electrolytic capacitor and tantalum capacitor is in their polymer electrolytes i.e. liquid and solid. Such properties as temperature characteristics and frequency characteristics are not as good with liquid electrolyte as with solid electrolyte because the variation in conductivity is great. In contrast, the recoverability of the oxide film is not as good with solid electrolyte as it with liquid electrolyte and so the development of a flow in the oxide film could easily resulting in a failure mode such as increase in leakage current or a short circuit, solid electrolyte capacitor do not have good ripple current resistance and charge discharge resistance. Since the range of tantalum capacitor are widely manufacture and used for most of applications.

Basic construction of Aluminum electrolytic capacitors

- The anode foil of aluminum electrolytic capacitor is 99.90 to 99.99% pure aluminum with a thickness of 40 to 110 μm.
- The surface of aluminum foil is increased by electrolytic etching in a hydrochloric acid or salt solution, thus increasing the surface are by 20 to 50 fold.

- The etched foil then undergoes anodic oxidation in a boric acid or ammonium salts of organic acid two form a dielectric oxide film on the surface of foil.

- The film increases proportionally to the formation voltage (approximately 1.3 nm per volt) and it can be freely formed in thickness from 1nm up to 900 nm with stand voltage: approximate

700 volt. the minimum film thickness in the film capacitor is 2 to 5 um. The dielectric constant of the anode film is approx . 8.5.

- The cathode film is 99.3 to 99.7% pure aluminum with a thickness of 20 to 50um and as with anode foil. Is it also etched. However the cathode foil does not undergo forming.

- The cathode foil used in capacitor act as a current carrying element and contact medium to the liquid polymer electrolyte.

- The electrolytic paper is then sandwiched between the electro foil and they are wound together to form a wound element.

- Electrolytic paper serves as a current carrying agent per electrolyte it also act as keeping agent to avoid short circuiting between cathode and anode and to achieve necessary voltage strength.

- The wound element is then impregnated with a liquid driving polymer electrolyte and it becomes to internal elements.

- This internal element is placed in an aluminum case with a bottom and top is covered with a sealing element.

Why volumetric efficiency is high

i)	Capacitance ‘C’ is directly proportional to Surface Area ‘A’.
ii)	Capacitance ‘C’ is directly proportional to Dielectric Constant ‘C’.
iii)	Capacitance ‘C’ is inversely proportional to distance.

By increasing the working area of a foil and reducing the distance thickness of oxide layer, we can achieve high volumetric efficiency.

Etching: for getting maximum capacitance per unit area etching process is important. Etching is the process in which area is increased by keeping its physical area same.

For Achieving maximum Capacitance how to reduce distance:

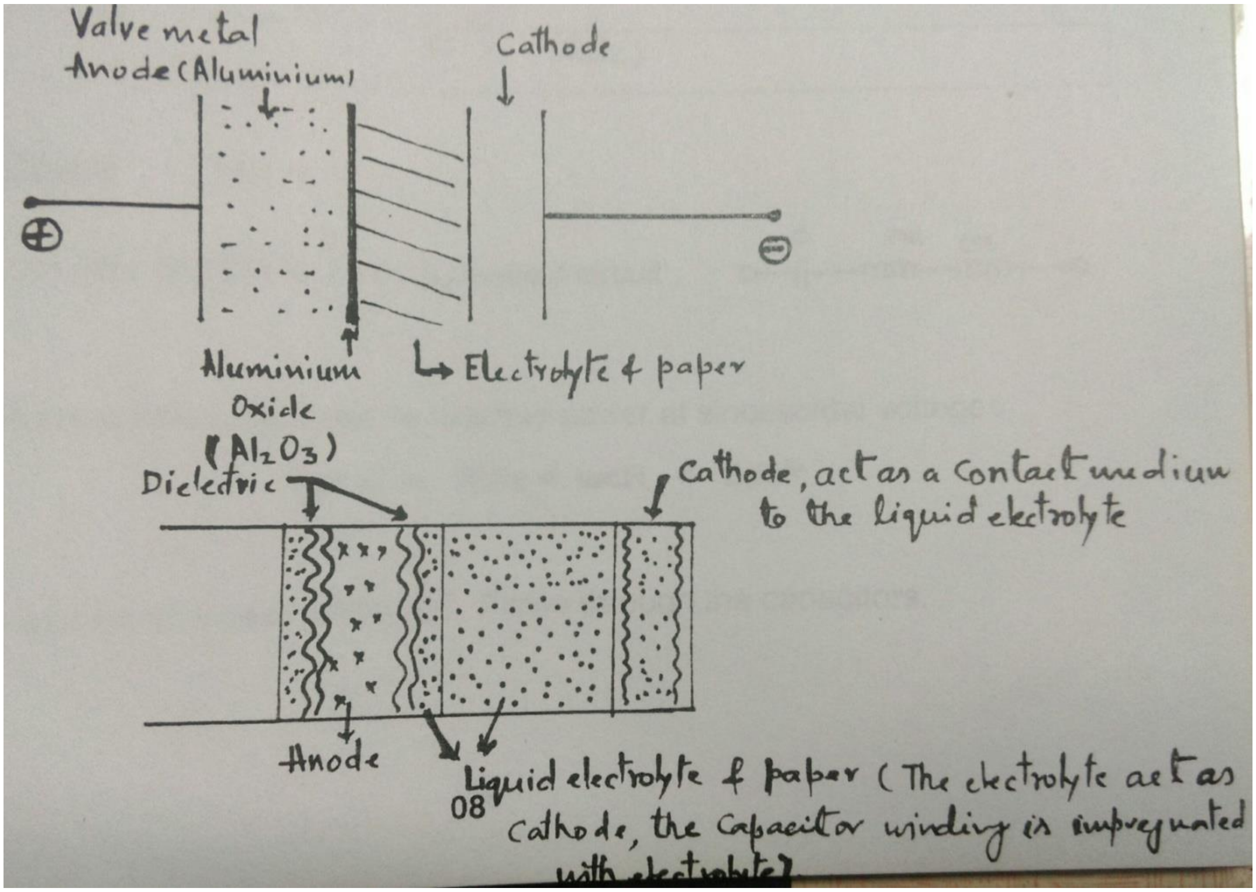
- The aluminum oxide film a generated by anodic oxidation.
- The thickness of the film grows practically proportionally to the applied forming voltage.
- For safety reason the final farming voltage is chosen higher than the rated or picks voltage value.
- The film thickness is approximately 1.3 nm per volt i.e. even with high voltage capacitor,a layer distance of only 0.7um can be expected .

- The minimum thickness of a paper dielectric for example 6 to 8 μm.
- Aluminum oxide in particular has the advantage of being design in thinner layer as compare to other dielectric because of its un usually high permissible operating field strength of approx 800MV/M.

<u>Parameter's of capacitor :-</u>

Capacitance: It is determined on the basis of resistance of capacitor or storage capacity when charged with DC voltage.

- Normally impedance basis is followed. Meters actually measure capacitive impedance which is proportionally covered to` C.' For general application measurement is carried out at 100Hz and 0.5v r.m.s.
- At low temperature capacitance decreases since viscosity of electrolytic increases reducing its conductivity. (Surface area will be affected).
- At high temperature capacitance increases since viscosity of electrolyte decreases, increasing its conductivity.



$C = Q/V$ where, Q = Charge in coulombs

V = Voltage in Volts.

$C = 8.854*10^{-8} AK/t$ (μF)

Where, A = Area in cm^2

T = thickness of dielectric

K = Dielectric constant

$K= 1$ for vaccum

3 to 8 for Mica

81 to 1200 for Ceramics

2 to 6 for paper

8.5 for Al_2O_3

Energy stored ‘W’ = ½ CV^2 watts-sec.

Dielectric Strength = 3KV/mm for Vacuum & 800KV/mm for Al_2O_3.

- Lower the rated voltage and more foil are etched.
- **Frequency effect:-** Capacitance decreases with increase in frequency.

Dissipation factor: TAN$

- It is the ratio of ESR to Xc in equivalent circuit.
- Or Ratio of effective power to reactive power at sinusoidal voltages

$$TAN\$ = R/Xc = wcR = 2\pi fcR$$

- Its measure of losses when AC flows through the capacitors.

- Normally, current in capacitor leads to voltage by 90 C but practically this is not achieved.

- The angle so lost is called loss angle and the tangent of this loss angle is called tan $.

- At low temperature tan$ increases because viscosity increases electrolyte.

- At high temperature tan$ decreases because viscosity decrease and resistivity decreases in electrolyte.

- At high frequency tan $ is high because property of electrolyte change at high frequency .

QUALITY FACTOR Q = 1/TAN$=Xc/R

TAN $ /ESR /QUALITY factor depend on following

- Electrolyte resistivity and viscosity, foil properties , contact resistance of lead tabs , unparallel winding , paper density etc.

IMPEDENCE: It is determined from the series connection of the following individual resistance.

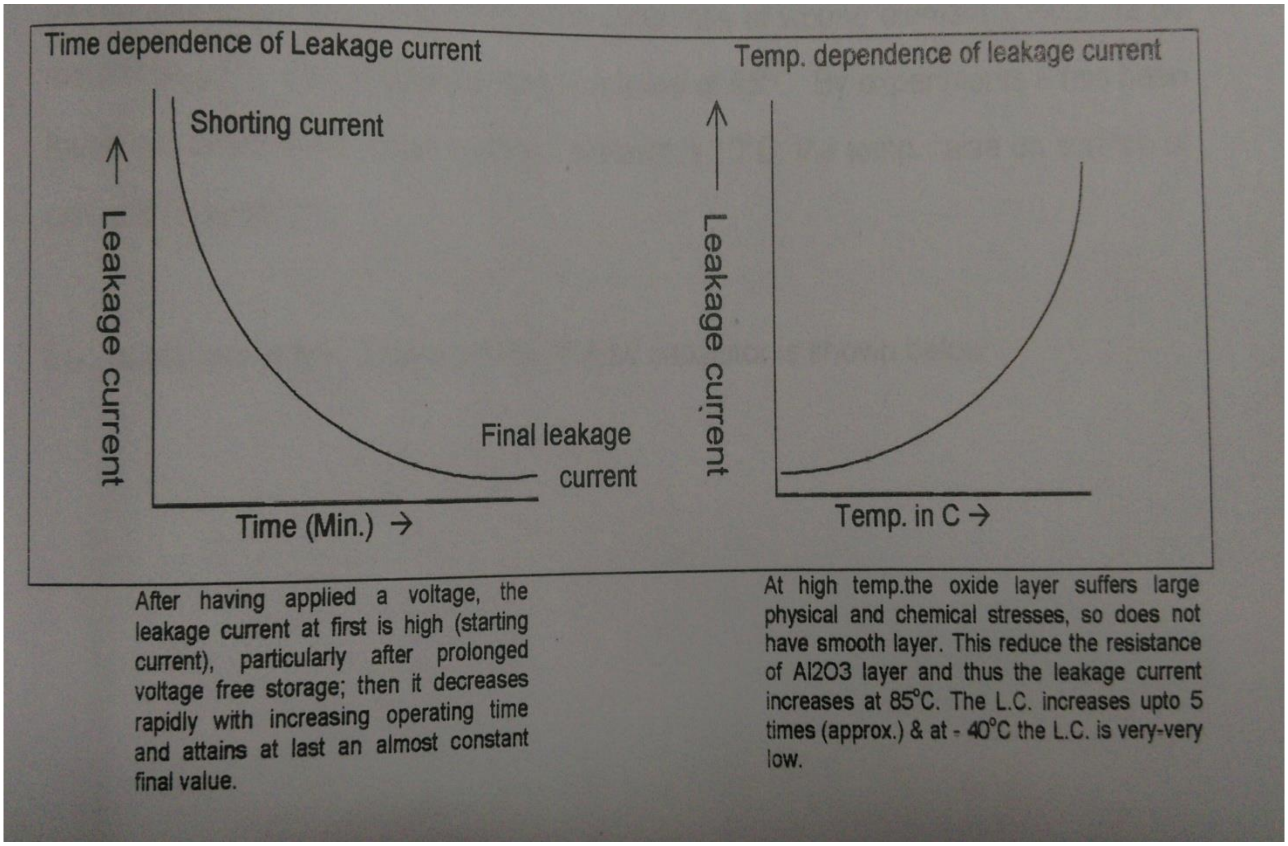
- Effective reactance Xc (1/wc) of ‘C’
- Ohmic resistance of Capacitor ‘R’(ESR)
- Effective reactance XL (wl) of inductance of wdg.
- Xc and Xl are dependent on frequency.
- ESR is temperature dependent (increases at lower temp.)
- Total resistance (Impedance) is dependent on freq. and temp.
- At lower frequency ‘Z’ is more

  Xc is Low (Xc =1/πfc).

- Z reduces with increases in frequency till it is equal to electrolytic resistance.
- Further increase in freq. Resonance minimum is formed.
- Inductive reactance XL(=WL) become operational when frequency increase to very high magnitude.

LEAKAGE CURRENT:

Due to special feature of the Al_2O_3 layer, servicing as dielectric a small current, the so called Leakage current flows even after applying DC voltage for a longer period. The leakage current is thus considered to be the measure for quality of capacitor.



RIPPLE CURRENT

The term ripple current means the r.m.s value of the alternating current with which a capacitor is loaded.

The max permissible value depends on

a) Ambient temp.
b) Capacitor surface area (cooling area)
c) The dissipation factor tan $ (or ESR)

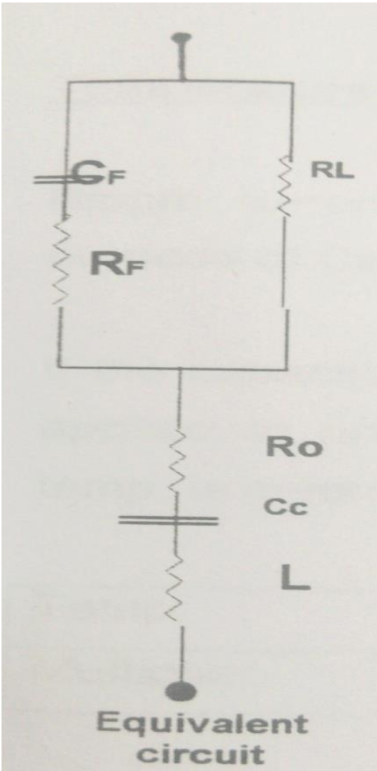
d) A.C frequency (to some extent).

When ripple current flows in a capacitor, the heat is produced inside the wound element. The heat produced will be due to watt loss.

WATT LOSS ‘W’ = 1 ESR

The heat produced due to watt los cause the increase in temp. of wound element. If the temperature inside the wound element goes beyond 95c. then the life of cap.will be reduced drastically. This means the temp. rise of wound element should not be more than 10c when ripple current Is applied 85c. by experiments it has been found that when temp. rise of wound element is 10c, the temp. raise on surface of can is 3c (at 84c).

Equivalent circuit an Aluminum electrolytic capacitor is shown below :-



CF : Capacitance of anode oxide film.

Cc: Capacitance of cathode.

RF: Equal series resistance of anode oxide film

Ro: Composite resistance of electrolyte and electrolytic paper.

RL : Resistance of leakage current

R: RF +Ro combined resistance equivalent series resistance(ESR).

The heat generated when the ripple current is applied to capacitor is given by

$$W = I^2R + V.I_L$$

Where I is the ripple current and IL is the leakage current since I is much greater than IL, so IL can be neglected

$$W=I^2R$$

The following equation is valid for obtaining the conditions under which internal heat generation and heat radiation become balanced.

$$\mathbf{W = I^2R = B.S.\Delta t}$$

Where,I = Ripple current (Amp.)

R = ESR (ohms)

B = Heat radiation factor (watt/'C cm)

Δt = temp. raise due to ripple current.

S= Surface area of case (cm2)

The value of B differs by case size. But the values are almost between 0.0007 to 0.0012.

Also tan$=WCR

R= tan $/We = Tan$/2πfc

Where f is the frequency in Hz and C is the capacitance in farad.

$\Delta t = I^2 \tan\$/B.S.WC = I^2 \tan\$/2nfc.B.S$

Temperature correction factor for ripple current

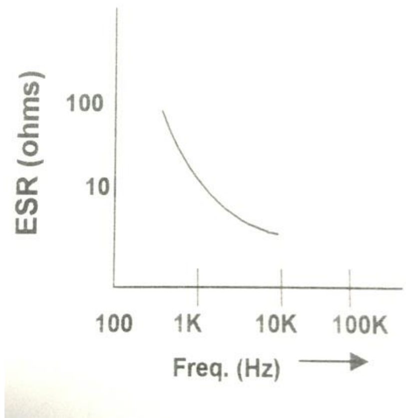
Ripple current is normally specified at maximum operating temp. (for general purpose of Cap. It is specified at 85°C).

If the capacitor is operated at some other temperature then the correction factor can be applied to ripple current. Corrective factor (multiplier) of ripple current at some temperature is given below:

Temp.	84 deg. Celcisus(°C)	70 °C	56 °C	41 °C
Multiplier	1	1.7	2.1	2.5

Frequency correction factor for ripple current

As shown in fig. The resistance (ESR) which effect heat generated by ripple current, tends to decrease as the freq. increase and therefore it can be considered that , higher the freq. the easier it is to flow of ripple current.



As far as frequency is concerned, the ripple current is normally specified at 100 Hz or 120 Hz.

To calculate the ripple current at some other frequency ‘f’; the following formula should be used

$$I^2R = I^2F * RF$$

I = Ripple current at 10 Hz /120 Hz

R = ESR at 100 Hz/120 Hz

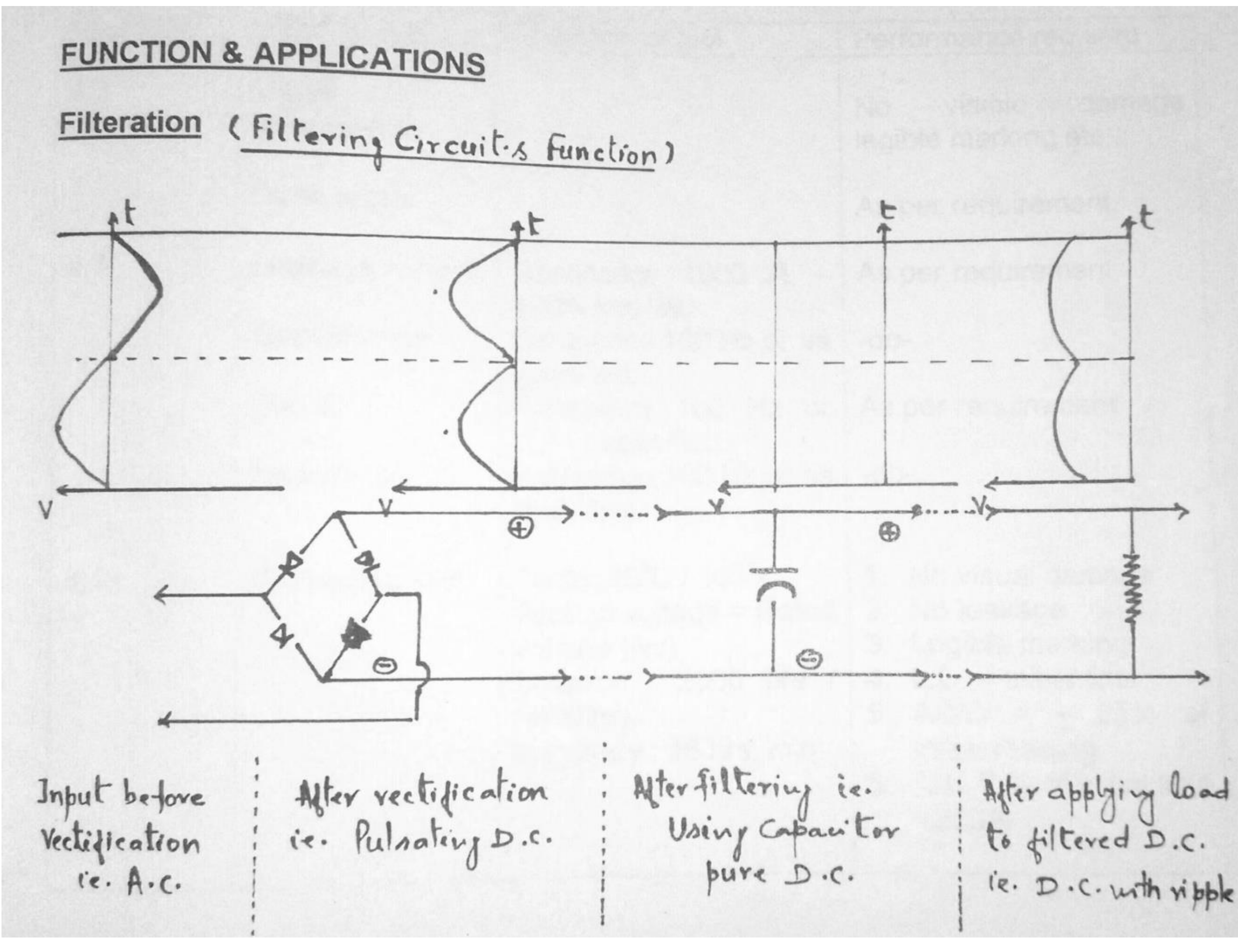
If = Ripple current at freq. F Hz.

Rf = ESR at 100 Hz/120 Hz.

Correction factor (Multiplier factor) of ripple current at some frequency is given below

FUNCTION & APPLICATIONS

Filtration



APPLICATIONS:

General purpose: All types of linear power supply.

Industrial Grade: UPS, Motor drives,welding equipments

Low impedance: Medium & high frequency small power supply.

Low leakage: Timer, flasher, charger & discharge and oscillator circuits.

Long life: Circuits where long life and high temp. is required.

Bipolar: Speaker crossover network in Hi-Fi audio system, Horizontal correction circuits in T.V & VIDEO A.C. motor starting, unknown polarity circuits.

Life of electrolytic capacitor

Expected life is affected by operation temp. Generally, each 10'C reduction in temp. will double the expected life . So use capacitors at the lowest possible temperature below the max. Guaranteed temperature.

The formula for calculating expected life at lower operating temp. is as follows:

$$L2 = L1*2^{(T1-T2)/10}$$

WHERE:-

L1 is guaranteed life at temp. T1' °C

L2 is expected life at temp. T2'°C

T1 = Maximum operating temp.

T2 = Actual operating temp. + temp. rise due to ripple current.

Conducting polymer:

Conducting polymers are novel class of compound and find applications in various fields such as battery, sensors , biological, micro electronics etc. In capacitor technology electrolytes are basically conducting polymer (polyester). In general it is defined as the solvent along with some additive which able to pass current in controlled manner because it passes some resistivity, to control the leakage current and other electrical parameters like ESR. Tan$ etc. in Alcos i.e. Aluminum Electrolytic Capacitors. Suitable matching of electrolyte resistivity is desirable. Normally in capacitor industries Electrolytes (conducting polymers) made by mechanism of poly condensation reaction and simultaneously followed by polymerization reaction. Ethylene glycol is a major constituent along with high conducting Ammonium salt's of organic acid and finally derived conducting polymer recipe. There are number of additives which are used in the development of such kind of polymer. Such as organic acid i.e. pH modifier, Hydrogen absorbing compounds, low viscosity solvents, spark voltage additive . Chemistry of important ingredients is discussed later on separately.

Function of conducting polymer

The electrolyte of aluminum electrolytic capacitor has not only the function of the cathode but also that of recovering the oxidized film. Therefore, even if a shock like electric pulse is given, it absorbs the shock and recover's the film quickly, and leaves no trouble such as short circuit and other capacitors do.

But as time passes, electrolyte which functions as cathode, dissociates and evaporates until it dries up. Moreover compared with capacitors, aluminum electrolytic capacitors have greater resistance because they also have the resistance of electrolyte and foil. So when AC run's due to the resistance, they generate heat themselves and shorter their lives.

Aluminum electrolytic capacitors are easily affected by heat, for they contain liquid electrolytes. The experiment show that the life of capacitor life is doubled when the temperature is 10 °C is lower, and shortened one half when the temperature becomes 10°C higher. This has been proved to be right theoretically, and it is generally called the "Low of Arrhenius" because it is very similar to Arrhenius chemical reaction speed. The showing is the formula.

$$\mathbf{L_2 = L_1 A^{(T_1 - T_2)/10}}$$

L1 : Effective life at the maximum operating temperature

L2 : Effective life at the normal operating temperature

T1 : Maximum operating temperature of the capacitor (c)

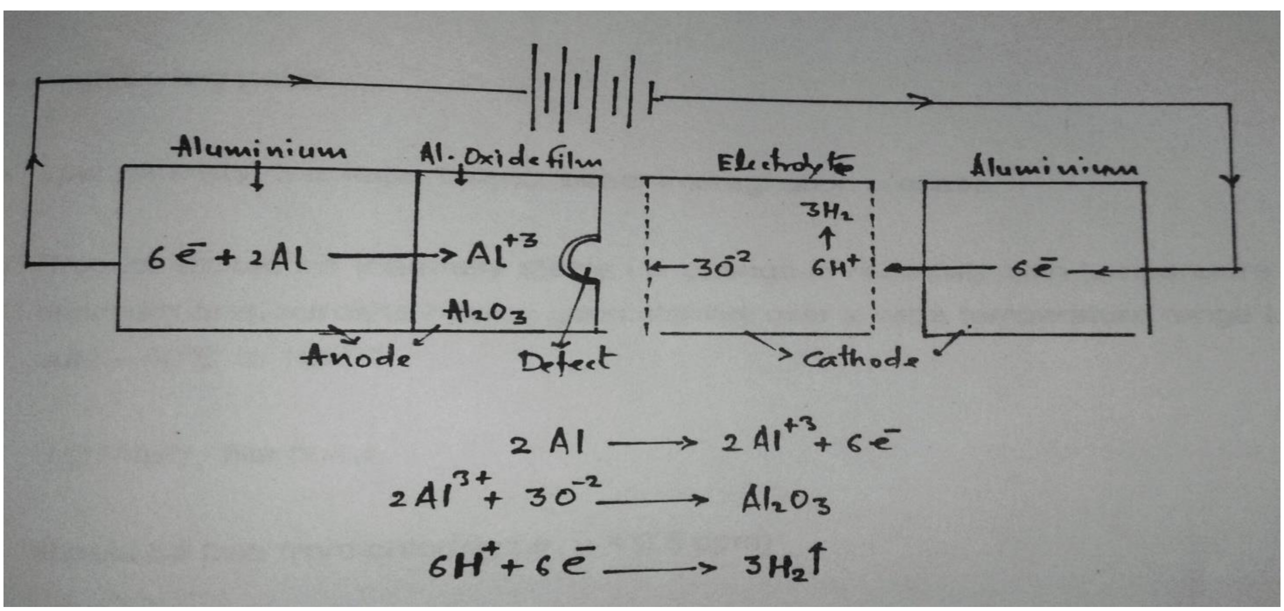
T2 : Actual operating temp. + temp rise due to ripple current

A : A Coefficient of temperature acceleration.

NOTE : A coefficient of acceleration is, if it Is below maximum operating temperature, A=2. A coefficient of acceleration is expressed as the change rate of equivalent series resistivity of capacitor.

Self repairing mechanism in Al. Elect. Cap.

The self repairing action of Al. Elect. Cap. Quickly repairs film defects by the mechanism show in fig. below



The oxidation at the anode will cause reduction at the cathode, resulting in the generation of hydrogen gas (H_2). When used under conditions of guaranteed ranges, the hydrogen gas generated is extremely small. This generated gas is dissipated either by the depolarization action of the electrolyte or through the sealing element so there is no problem.

Characteristics of good electrolyte's:

- The electrolyte should have low specific resistance in order to restrain generation of heat of itself. It should not affect rubber seal and aluminum.
- Electrolyte should have low vapour pressure at high temperature.
- High spark voltage
- pH should be neutral or nearby 7.0
- high boiling point
- Low viscosity. It is important for better impregnation process.
- Product should be thermally stable i.e. change in resistivity with temperature is minimum or electrolyte have a good stability over a wide temp range i.e. up to -40°C to 150°C.
- Should be free from chloride i.e (<0.5 ppm)
- High flash / fire point.
- Very low freezing point.

- It contain very less impurities i.e Fe,SO_4,Pb etc. ppb or ppm level.
- Non reacting with moisture.

Useful ingredients and their chemistry:

Ethylene glycol is main solvent used in development of conducting polymer. Apart from Ethylene glycol, methyl glycol V-butyrolactone, diethylene glycol, glycerol, Dimethyl foramide , N-methyl pyrrolidone etc. are most important . Their importance, important specification, chemical preparation and important reaction ,use's are given individually.

List of solvent, used in development of conducting polymer

Ethylene glycol	Y-Butyrolactone
Diethylene glycol	Dimethyl formamide (DMF)
Methyl glycol	N-Methyl pyrrolidone
Glycerol	Triethylamine
Benzyl alcohol	

Similarly following purified organic acids and its ammonium salts for conducting polymers (for electrolytic capacitor) are important & are highly purified which especially corrosive substance , that effect the capacitors anode and cathode.

There are highly noted because of their high quality as components substances for electrolytes and also as chemical formation agents.

If they are used as electrolytes, compounds with ammonium are recommended for ordinary purposes since ammonium compounds are preferable for preventing pollution and also for labour rationalization.

List of chemicals which are useful for development of conducting polymers

Adipic acid	Ammonium adipate
Benzoic acid	Ammonium benzoate
Azelaic acid	Ammonium azelate
Sebacic acid	Ammonium sebacinate
Dodecanedioic acid	Ammonium dodecanediote
Citric acid	Picric acid
P-nitrobenzoic acid	paranitrophenol

CHEMISTRY OF INGRADIENTS- SOLVENTS

<u>Glycols</u>

GLYCOLS: (Dihydric alcohols containing two hydroxyl group)

Simple glycol

$C_nH_{2n}(OH)_2$

Hydroxyl groups are attached

to unsubstituted hydrocarbon chain

Example- Ethylene Glycol

Polyglycols

$C_nH_{2n}On(OH_2)$

In this, intervening ether linkage is present in the hydrocarbon chain.

Up to either carbon atoms.lower poly-Glycols

e.g. Diethylene Glycol

Above Eight- higher Polygols

Ethylene Glycol (Ethane-1,2-diol)

$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

EG is a colorless, odorless, high boiling, hygroscopic liquid. It is completely miscible with water and many organic liquids. It markedly reduces the freezing point of water. It is insoluble in ether and is widely used as a solvent.

The high boiling points and high solubility of polyhydric alcohols in matrix are due to hydrogen bonding involving all hydrogen groups. It undergoes the reaction typical of a monohydric alcohol.

<u>Some important specifications</u>

Mol . wt.	62.06
Sp. Gravity /20 °C	1.1154
B. pt. °C	197.6 °C
Vapour pressure at 20 °C	< 1.3 pa
Melting point	-13.0 °C
Viscosity at 0 ,20,40 °C	51.36,19.82 and 9.21 c.p resp.
Flash point , °C	116

Important Reactions

i) The reaction of EG with dicarboxylic acids to form linear polyesters is of immense commercial importance.

$$2n\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + n\ HOOC(CH_2)XCOOH \longrightarrow$$

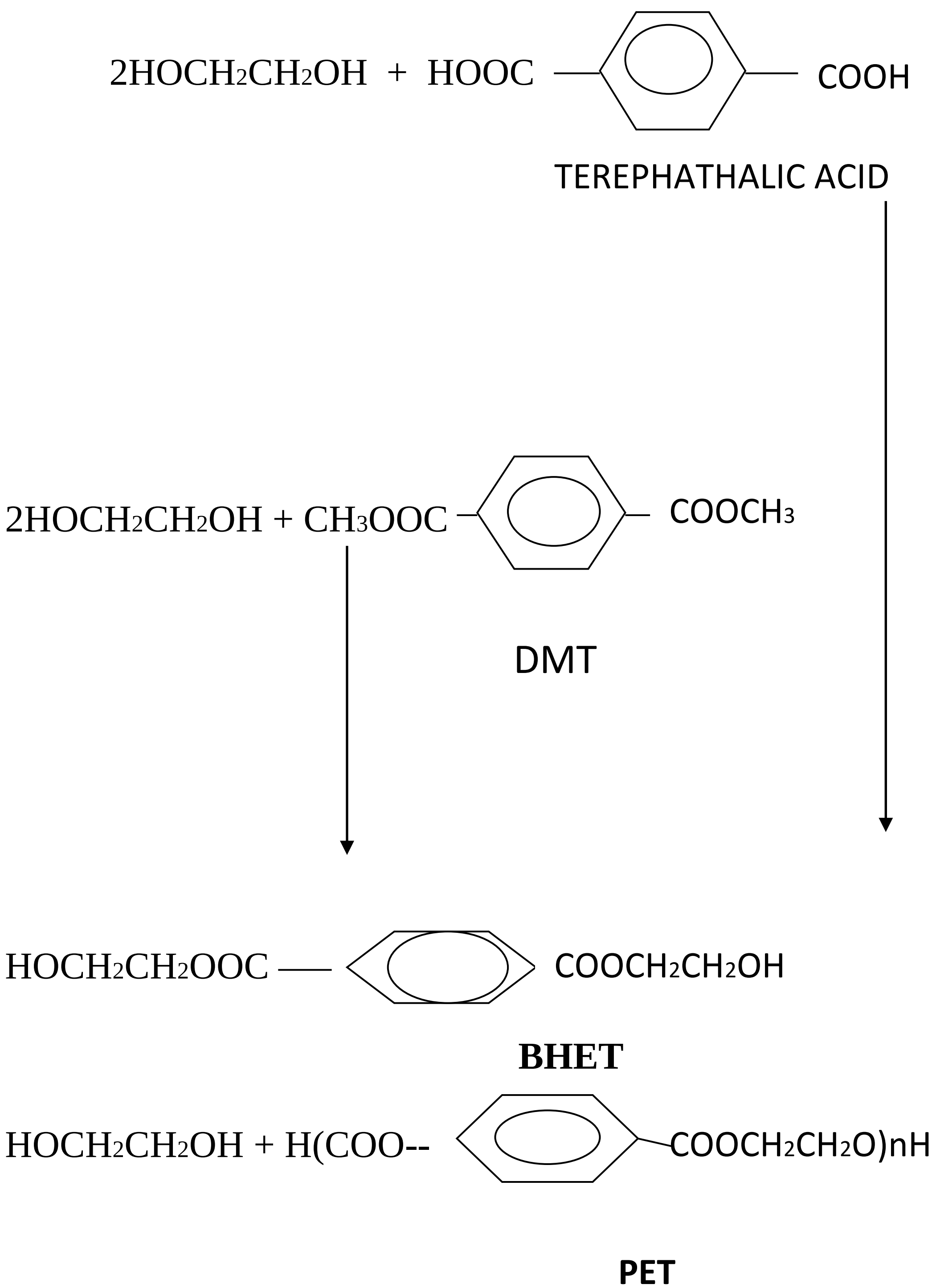
$$[HOCH_2[CH_2OOC(CH_2)XCOOH_2]CH_2OH]n + 2nH_2O$$

ii) when treated with organic acids or inorganic oxygen acids,the mono or diesters are obtained , depending upon relative amounts of glycol and acids e.g.

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2\ CH_3COOH \longrightarrow \begin{array}{l} CH_2OCOCH_3 \\ \\ CH_2OCOCH_3 \end{array}$$

Glycol di Acetate

iii) Ethylene glycol is esterified with terepthalic acid or transesterified with dimethyl terephthalate to form bis-(hydroxyethyl) terephthalate (BHET).



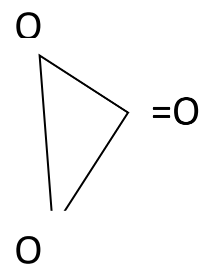
BHET Polymerizes at high temperature and low pressure over an antimony trioxide catalyst to poly ethylene terepthalate (PET).

iv) Transesterification with diethyl carbonates produces ethylene carbonate.

CH_2OH

$+ C_2H_5OCOOC_2H_5 \longrightarrow$

CH_2OH

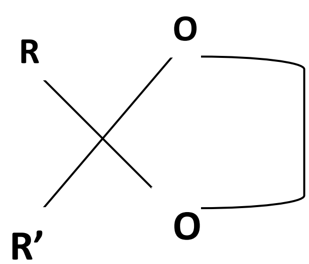


$+ 2C_2H_5OH$

V)

V) Reaction with aldehydes or ketones under acid conditions form 1,3 dioxolanes.

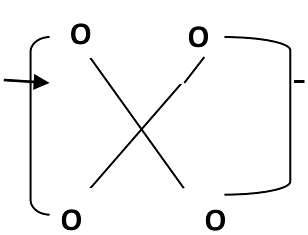
$HOCH_2CH_2OH + RCOR' \longrightarrow$



$+ H_2O$

Vi) A chelate can be prepared with boric acid.

$2OHCH_2CH_2OH + H_3BO_3 \longrightarrow$



H^+

$+ H_2O$

vii) Glycol is not readily dehydrated to acetaldehyde. However, in presence of dehydrating agent it gives acetaldehyde.

viii)

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{ZnCl_2} CH_3CHO + H_2O$$

ix) When heated with dehydrating agent like phosphoric acid, diethylene glycol is obtained.

$$2HOCH_2CH_2OH \longrightarrow HOCH_2CH_2OCH_2CH_2OH$$

DIETHYLENE GLYCOL

USES

1) It is used as a non-volatile antifreeze for liquid cooled motor vehicles.
2) It is used in the manufacture of polyester fiber and film.
3) It is also used as a heat transfer fluid, in aircraft and runway deicing mixtures, as a dehydrating agent for natural gas , in motor oil additives and as an additive in the formulation of inks , pesticides, wood stains, adhesives and many other products.

4) A minor but important use for high purity EG is as a solvent and suspending medium for ammonium pent borate, the conductor is practically all electrolytic capacitors.

Purification

Very hygroscopic and also likely to contain higher diols. Dried with calcium oxide, calcium sulphate, magnesium sulphate or sodium hydroxide and distilled under vacuum. Further dried by reaction with sodium under nitrogen refluxing for several hours and distilling. The distillate was then passed through a column of linde types 4A molecular sieve and finally distilled under nitrogen, from more molecular sieve. Fractionally crystallized.

Methyl Glycol (monomethyl ether of glycol)

$$HOCH_2CH_2OCH_3$$

When ethylene oxide is heated with methanol under pressure, methyl cellosolve is formed.

$$CH_2\text{-}CH_2 \quad + CH_3OH \dashrightarrow HOCH_2CH_2OCH_3$$

METHYL CELLOSOLVE

Cellosolve are very useful as solvents, since they contain both the alcohol and ether functional groups.

Some important physical characteristics

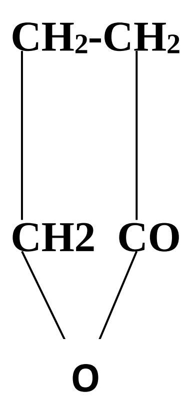
Mol. Wt.	76.08
Density	0.9662
Boiling pt.	124.4 °C
Melting point	-85.3 °C

When ethylene oxide is treated with cellosolve produce carbitols e.g.

$$HOCH_2CH_2OCH_3 + \overset{O}{CH_2\text{-}CH_2} \rightarrow HOCH_2CH_2OCH_2CH_2OCH_3$$

It is also used as a solvent in electrolytes. It is used for decreasing viscosity of electrolytes . Addition of methyl glycol to electrolyte lowers the freezing point of electrolyte and consequently lowers the resistivity while retaining high voltage capabilities.

Y-Butyrolactone (Dihydro-2(3h)-furanone)



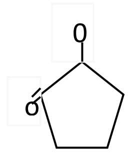
Y-Butyrolactone: Y-Butyrolactone , dihydro-2(3H)—Furanone was first synthesized in 1884 via internal esterification of 4-hyroxybutyric acid . At present, two routes are used for commercial production. The dehydrogenation of butanediol and more recently, hydrogenation of maleic anhydride to tetrahydro furan and butyrolactone .the properties are given in table 5.

Physical and chemical properties of Butyrolactone.

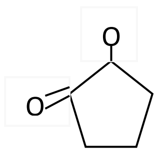
Properties	
Flash point , open cup, °C	98
Fire point	99
Freezing point, °C	-44
Specific gravity	1.128
Refractive index	1.4361
Viscosity	1.74
Dielectric constant at 20 °C	39.12
Heat capacity at 20 °C	1.61
Melting point	-45 °C

Some important chemical reactions

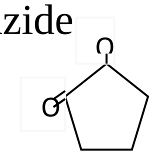
i) With alcohols and acid catalysts, esters of 4-hyroxybutyric acid are formed rapidly at room temperature. As with water equilibrium strongly favors the lactones. Attempt to distill the mixtures ordinary result in complete reversal to butyrolactone and alcohols.

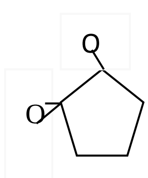
 + ROH → $HO(CH_2)_3COOR$

ii) When butyrolactone and alcohols are heated for a long time at higher temperature in the presence of acidic catalysts, 4-alkoxybutyriesters are formed.

 + 2 ROH → $RO(CH_2)_3COOR + H_2O$

iii) Hydroylamine adds to give a hydroxamine acid and hydrazine to give hydrazide

 + $HONH_2$ → $HO(CH_2)_3CONHOH$

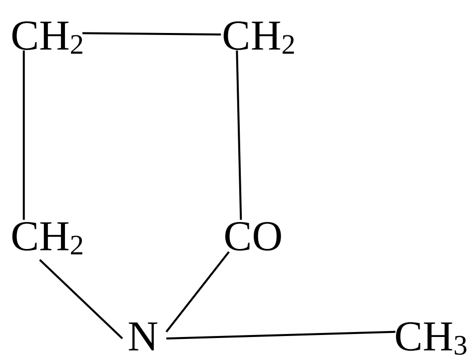
 + NH_2NH → $HO(CH_2)_3CONHNH_2$

v) Butyrolactone reacts rapidly and reversibly with ammonia of an amine to from 4-hydroxybutyramides, which dissociate to butyrolactone and amine when heated.

Butyrolactone is used as an intermediate with ammonia and methylamine to manufacture 2- pyrrolidinone and N-methyl 2-pyrrolidinone respectively.

It is also a solvent for agriculture, chemical, polymers, dyeing and printings. Small amounts are employed in various organic synthesis. The infra-red absorption region of the carbonyl group (C=O) stretch) is Y-lactones is 1780-1760 cm, it is used as a solvent in electrolytes mainly for those electrolytes which are being used for 105C because of its high boiling point.

N-METHYL PYROLIDONE



N –methyl pyrrolidone in electrolyte mixture reduce the water activities without destruction of the borate complex which is responsible for conductivity and forming ability. It is used in development of low/middle voltage electrolyte and it is also suitable for 105c applications.

Triethylamine

$(C_2H_6)_3N$

Some important physical characteristics

Mol. wt.	101.18
Melt. pt.	- 116 °C
Boil. pt.	88.9 °C
Density	0.725
Flash pt.	-6 °C

It is used in electrolytes to increase ph of electrolytes.

N-Methylformamide (NMF)

$HCONHCH_3$

Some important physical characteristics

Mol. wt.	59.06
Melt.pt.	-40°C
Boiling pt.	180- 184 °C

Density	1.012
Flash pt.	98 °C
Viscosity (-60C)	20 c.p.

It is used as a solvent in electrolytes. It forms a stable electrolyte of low viscosity and high conductivity.

Dimethyl Formamide (DMF)

$$HCON(CH_3)_2$$

It is manufactured by reaction between methyl formate and dimethylamine.

$$HCO_2Me + Me_2NH \rightarrow HCONMe_2 + MeOH$$

It is a very good solvent for polar and non polar compounds, and it is used as formulating agent in conjunction with phosphoryl chloride.

Some important physical characteristics

Mol. Wt.	80.16
BOILING PT.	151 °C
Density	1.031
Flash pt.	57 °C

Chemical properties

Amides are hydrolyzed slowly by water , rapidly by acids and far more rapidly by alkalis'.

$$RCONH_2 + H_2O \rightarrow RCO_2H + NH_3$$

DMF decreases the viscosity of electrolyte but the electrolytes with tend to loose the solvent at a high temp. in view of the fact that the boiling point of DMF is relatively low than EG and the life of an electrolytic capacitor at a high temperature is not long.

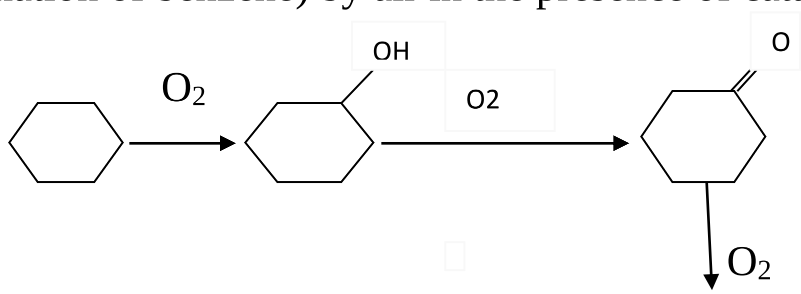
THE CHEMISTRY OF INGRADIENTS- SOLUT'S

Adipic Acid (hexanedioic Acid)

(1,4 – butanedicarboxylic acid)

$HOOC(CH_2)_4COOH$

It is prepared industrially by the oxidation of cyclohexane (from the hydrogenation of benzene) by air in the presence of catalyst e.g.



$HO_2C(CH_2)_4CO_2H$

Some important physical characteristics

Mol. Wt.	146.13
Melting pt.	153-153.1 °C
Boiling pt.	265/100 mm
Flash point	196 °C
Viscosity of melt	Temp. °C 160 193

Chemical Reactions

- Adipic acid is readily esterified and forms both mono and di esters. Acid catalyst are normally used but the reaction proceeds readily in the absence of catalyst at elevated temp. If water of reaction is removed or if large excess alcohol is employed.

  Other purification procedure includes crystallization from ethyl acetate and from acetone – petroleum ether, fusion followed by filtration and the melt and preliminary distillation under vacuum.

Ammonium Adipate

$$NH_4OOC(CH_2)_4CONH_2$$

Character	Crystal of colorless
Solubility	Highly soluble in water Soluble in E.G.16 wt.% at 20C Insoluble in D.M.F.

USES

One of most widely used chemicals having an excellent property against E.G and various properties suitable for use in forming .

Purification

1-Aminoadipic acid (anhydrous) , crystallized from water

Ammonium benzoate

$C_6H_5COONH_4$

CHARACTER: Crystal of colorless

Melting point 198 °C

Sublimation	At 160 C ,density 1.261
Solubility	Soluble in water 22.9wt. % Soluble in alcohol 1.66 wt. % Soluble in E.G. 20 wt. % Soluble in M.G.,D.M.F.,D.M.S.O.

Uses:

Used for middle or high voltage capacitors.

<u>Azelaic acid(nonanedioic acid)</u>

$HOOC(CH_2)_7COOH$

Azelaic acid is prepared industrially by the ozonolysis of oleic acid.

Mol wt.	188.22
Melting Pt.	109-111°C
Solubility	0.2/100g at 15- °C
	1.65g /100g at 55-°C

PURIFICATION

Crystallized from water (charcoal) or thiophene –free benzene . the materiel crystallized from water was fired by azeotropic distillation in toluene the residual to toluece solution was cooled and filtered. Precipitate being dried in vacuum over –purified by zone melting or by sublimation onto a cold finger at, 10 torr.

Uses:

It is used in the form of esters in hydraulic fluids and lubricants. Metal salts such as aluminum and lithium are used in grease

It is used as an Ionogen in electrolytes.

Ammonium Azelate

$$HOOC(CH_2)_7COONH_4$$

Character: Crystalline powder of light brown.

Solubility: Very soluble in water and alcohol

Soluble in E.G. 20 wt. % at 20 °C

Uses

Uses for middle or high voltage capacitors.

As this chemical can withstand a relatively high spark tension and its conductivity is high. It is gradually replacing Boron compounds and is used in high voltage capacitors and may also be used for high tension chemical forming. Since the number of carbon atoms in each molecule is odd. It displays unique properties.

Its crystal, being an acid salt, is very stable.

Sebacic Acid (Decanedioic acid)

$$HOOC(CH_2)_8COOH$$

It is prepared industrially by heating castor oil with sodium hydroxide

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COONa + NaOH$$
$$\downarrow$$
$$NaOOC(CH_2)_8COONa + C_6H_{13}CHOHCH_3$$

PHYSICAL CHARACTERISTICS

Mol Wt.	202-24
Melting pt.	135-137 °C
Water solubility	0.1g/100g at 15 °C

It is soluble in alcohol and ether.

Uses

Sebacic acid and its derivatives are used in plastic industries for plasticizers, alkyd resins, polyester resins, polyurethane and polyamide molding resins. The diesters are used as lubricants, thinner for castor oil lubricants and as stable plasticizers for polyvinyl chloride and other film forming polymers.

Purification

Purified via the disodium salt which after crystallization from boiling water (charcoal),was again converted to the free acid. The free acid was repeatedly crystallized from hot distilled water and dried under vaccum.

Ammonium Sebacinate

$$NH_4OOC\ (CH_2)_8COONH_4$$

CHARACTER: Crystal of colorless

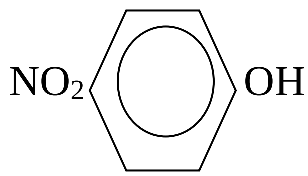
Solubility: soluble in water and alcohol

Soluble in E.G 12 wt. % at 25 °C

Uses

Used in middle and high voltage capacitors.

Para Nitro Phenol (4-Nitrophenol)



p-nitro phenol

Treatment of phenol with cold dilute nitric acid gives a mixture of 0 and p-nitro phenol.

Physical Characteristics

Mol wt.	139.12
Melting pt.	112 – 114 °C
Boiling pt.	278 °C

Chemical properties

Solubility in hydroxylic solvent depends on the power to form hydrogen bonds with the solvents, phenol can form these bonds and hence certain solubility in H_2O can be expected.

p-Nitro phenol is readily reduced to the corresponding amino phenol.

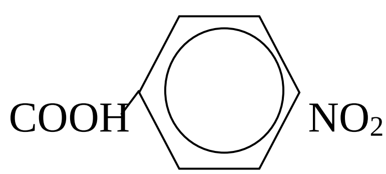
p-Nitro phenol give rise to two series of ester , one colored and the other colorless. The colorless series contains the benzenoid structure, where as the colored series contains the chromophore quinine.

Uses

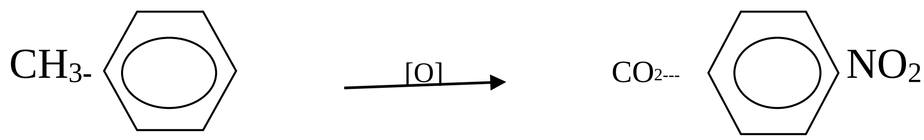
For absorbing hydrogen gas generated in negative pole.

Oxygen gas, as it has a tendency to attract electron and be become negatively charged due to its high electro negativity ,absorb hydrogen gas generated expelled O2 reacts with hydrogen to form H2O. The above reactions relieve the internal pressure inside the capacitor.

P-Nitrobenzoic acid



P-Nitrobenzoic acid may be prepared by oxidizing the corresponding nitrotoluences with acid dichromate.



Physical Characteristics

Mol. Wt.	167.13
M. pt.	239-241.1 C

Chemical reactions

The course of reduction of nitro compounds has been shown to take place through the following stages:

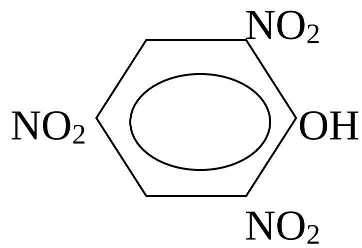
$CO_2HC_6H_4NO_2 \rightarrow ONC_6H_4CO_2 \rightarrow COOHC_6H_4NH_2$

The nature of the final product, however, depends mainly on the pH of the solution in which the reduction is carried out

Uses

Paranitrobenzoic acid is used as a hydrogen absorbing solvent in electrolyte because of the presence of NO2 ground which is reduce to NH3 by the H2(H2 is produced inside the capacitor).

Picric acid



When picryl chloride is boiled with water picric acid is formed

Mol. Wt.	229.12°C
Melting pt.	121-123 °C

Development of Conducting Polymer and its testing:

Preparation of conducting polymer :

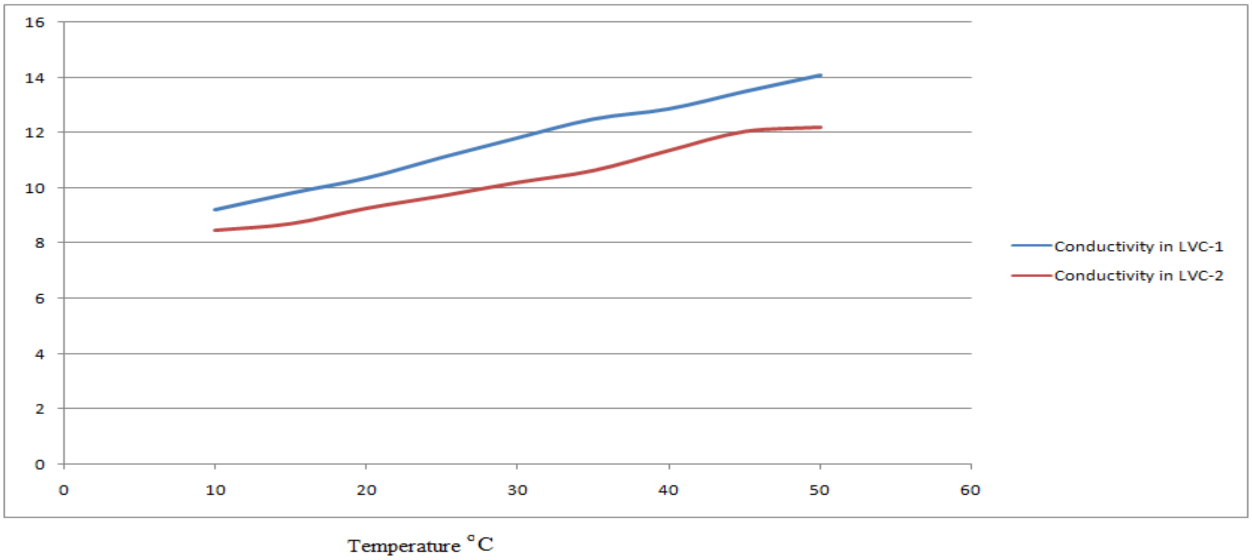
Initially fixed proportion of ethylene glycol, methyl glycol or water is to be mixed in reactor by maintaining temperature 65°C for 1 hour and then add additive except Hydrogen absorbing compound for mixing of matrix. Now allow the mixing of all ingredients along with solvent for 6 hour at 85°C raise temp. of double jacketed mixer/reactor so that resultant mixture reached at their boiling pt. When temp. of reactor is raised also add water absorbing compound. When resultant reached at boiling point, at this temp. Mixing is allowed only for 2-5 min. maximum and after that immediately transferred the electrolyte into storage vessel. Now it allow to cool down at room temp. in closed vessel. In finally obtain electrolyte, sample is taken for chemical analysis i.e. Resistivity, pH, chloride content, spark voltage is to be analyzed. Only after final approval of Q.A the resultant is allowed to use in process and it is called as conducting polymer. Direct heating of polymer should be avoided.

A Typical composition of derived polymer:

COMPOSTION	**LVC-1 (WT%)**	**LVC-2 (WT%)**
Solvent	51/39 E.G.,M.G./H_2O	54.00/38.0 E.G./H_2O

Conducting solute	5/3 Amm. Adipate	5.01 Amm. Adipate
pH modifier	2 Adipic acid	1.78/0.081 Adipic acid
Hydrogen absorbing compound	1	0.60

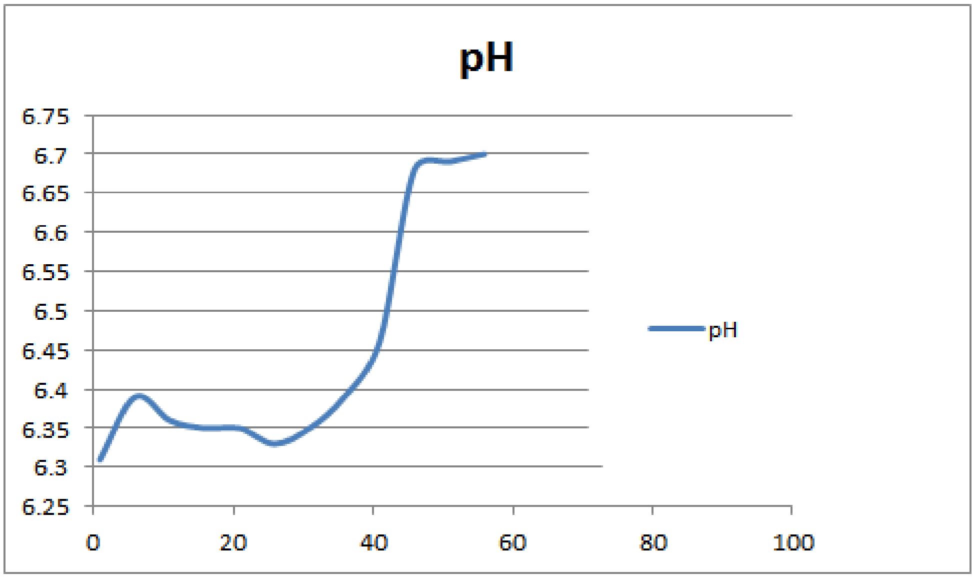
VARIATION OF CONDUCTIVITY OF LVC-1 & LVC-2 WITH TEMPERATURE



Conductivity Vs. Temperature

Temperature	Conductivity in LVC-1	Conductivity in LVC-2
10	9.21	8.47
15	9.81	8.71
20	10.36	9.27
25	11.11	9.72
30	11.82	10.21
35	12.5	10.64
40	12.87	11.37
45	13.5	12.06
50	14.09	12.21

VARIATION IN pH AT DIFFERENT TEMPERATURE (LVC-1)



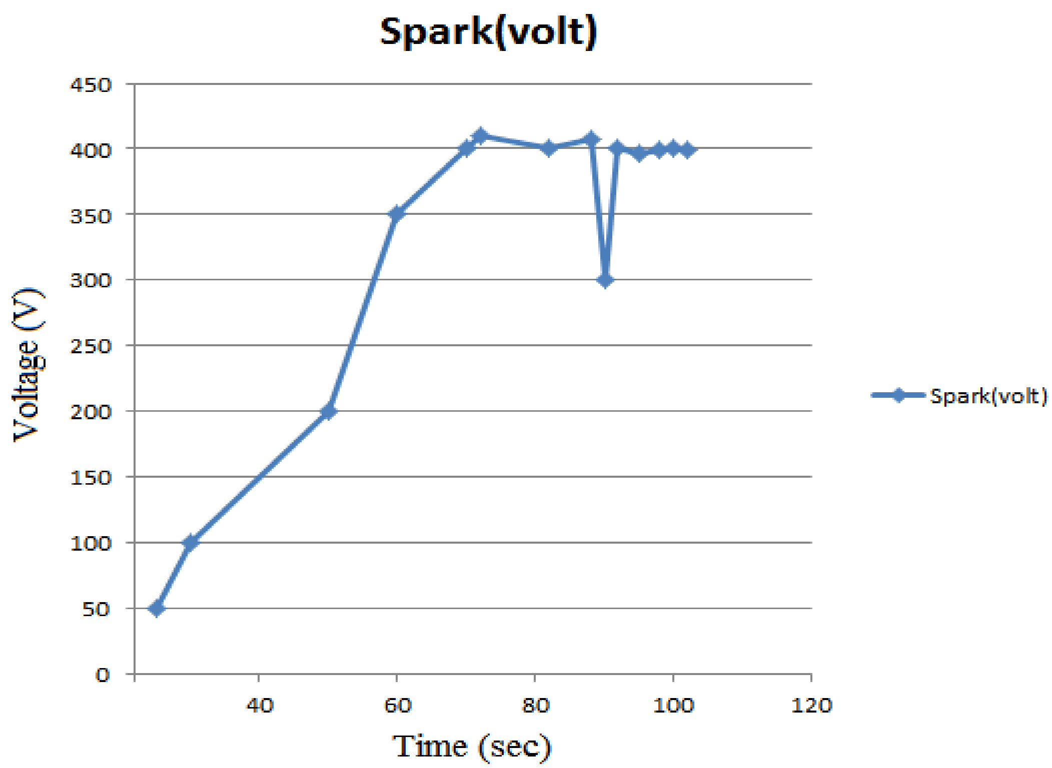
Temp -->

pH vs Temp.

Table -2

TEMP.	pH
30	6.31
35	6.39
40	6.36
45	6.35
50	6.35
55	6.33
60	6.35
65	6.39
70	6.46
75	6.68

MEASUREMENT OF SPARK VOLTAGE



Measured Voltage Vs. Time

Table 3

TIME (SEC.)	Spark Voltage(v)
25	50
30	100
50	200
60	350
70	400
72	410
82	400
88	407
90	300
95	400
97	399
98	399
100	401
102	399

EXPERIMENTAL DETAILS

(Technical data for LVC-1 &LVC-2)

GENERAL CHARACTERISTIC : Low voltage conducting polymer electrolyte.

Ethylene glycol/Methyl glycol/water based

CHARACTERISTIC of Polymer:	**LVC-1**	**LVC-2**
Appearance	: Light Yellow	Light Yellow
Working range	: 6.3-25Wv	6.3-25Wv
Temperature range	: -40-85 °C	-40-85 °C
Specific resistivity	: 80+/-5 ohm cm	100+/-10 ohm cm
Spark tension at 85 C	: 390-395 volt.	400-410 volt.
pH at 30 C	: 6-6.5	5.5-6.5

TEST RESULTS OF ELECTRICAL CHARACTERISTIC

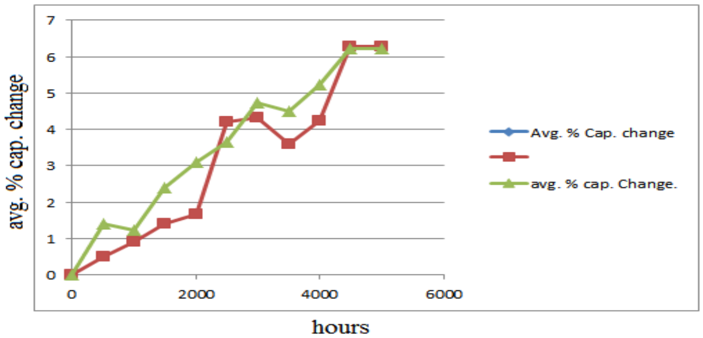
A) DESIGN OF CAPACITOR:

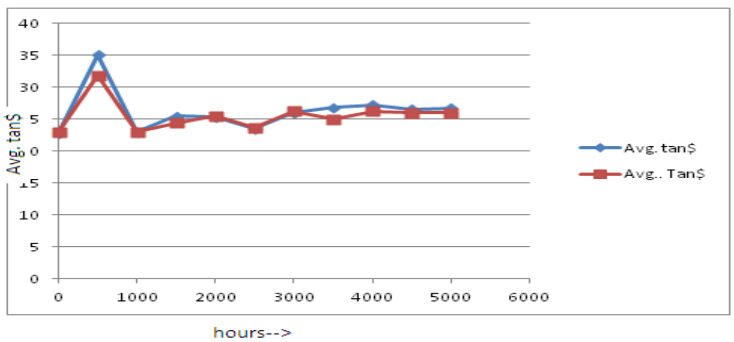
Anode foil	: U-134-9Vf
Cathode foil	:
Anode foil	:U-135-9Vf
Can size	: 12.5*21
Sealing Rubber	: EPDM
Capacitance	: 3300 μF
Working voltage	:6.3 volt.

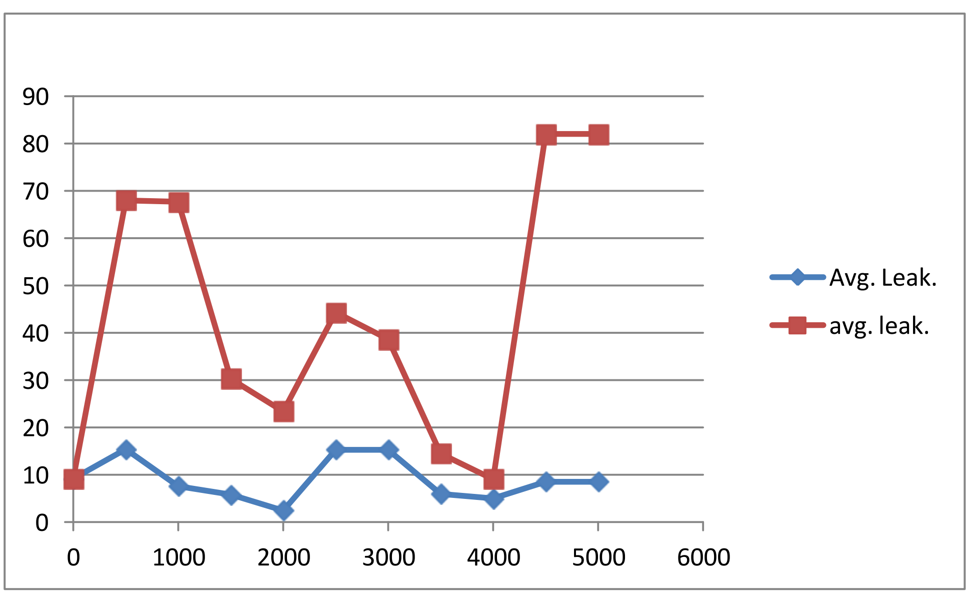
Life test results at 85 °C in LVC-1

ENDURANCE				SHELF		
HOURS	Avg. % Cap.change	Avg. tan$	Avg. leakage μA	Avg. % cap. change	Avg. tan$	Avg. leakage μA
0	0	19.71	17.81	0	19.76	16.83
500	0.51	16.71	15.41	1.4	16.61	75.01
1000	0.9	19.21	4.01	1.22	18.81	23.41
1500	1.4	19.98	3.60	2.4	19.81	21.69
2000	1.68	20.30	<0.01	3.1	19.61	45.21
2500	4.2	19.70	11.01	3.64	19.10	67.00
3000	4.32	21.41	12.61	4.72	21.00	263.81
3500	3.6	20.60	12.31	4.5	20.20	162.69
4000	4.24	22.11	21.42	5.24	21.09	151.40
4500	6.28	22.49	9.33	6.22	21.69	188.39
5000	6.29	22.81	12.51	6.23	21.81	301.79

ELECTRICAL PARAMETERS OF CAPACITORS(LVC-1)



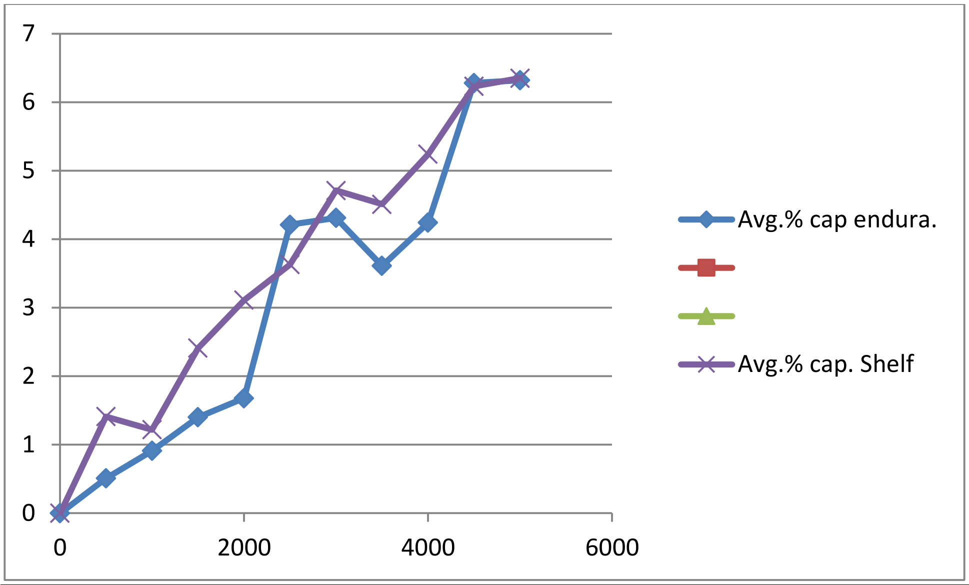




HOURS→

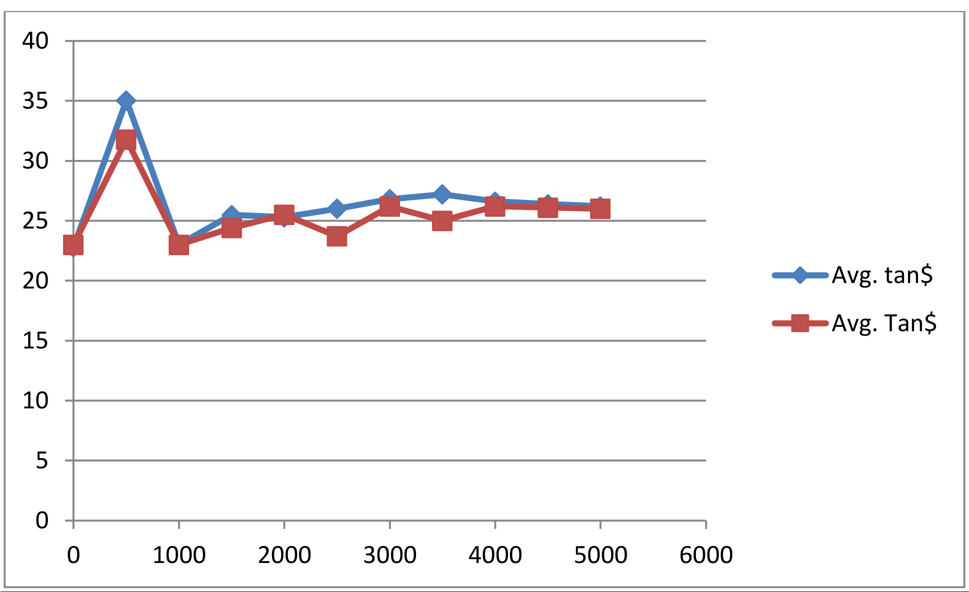
Avg. Leakage Current Vs. Hours

ENDURANCE				SHELF		
HOURS	Avg. % cap. change	Avg. tan$	Avg. Leakage uA	Avg. % cap. change	Avg. tan$	Avg. Leakage uA
0	0	22.82	9.16	0	23.01	9.16
500	0.51	35.04	15.41	1.41	31.79	68.01
1000	0.91	23.01	7.61	1.22	23.01	67.71
1500	1.40	25.49	5.81	2.41	24.4	30.31
2000	1.68	25.3	2.51	3.11	25.51	23.41
2500	4.21	26.01	15.31	3.63	23.71	44.31
3000	4.31	26.81	15.30	4.71	26.20	38.61
3500	3.61	27.21	6.01	4.51	25.01	14.5
4000	4.24	26.61	5.01	5.24	26.21	9.1
4500	6.28	26.39	8.63	6.23	26.10	82
5000	6.32	26.21	8.74	6.35	26.01	85.74

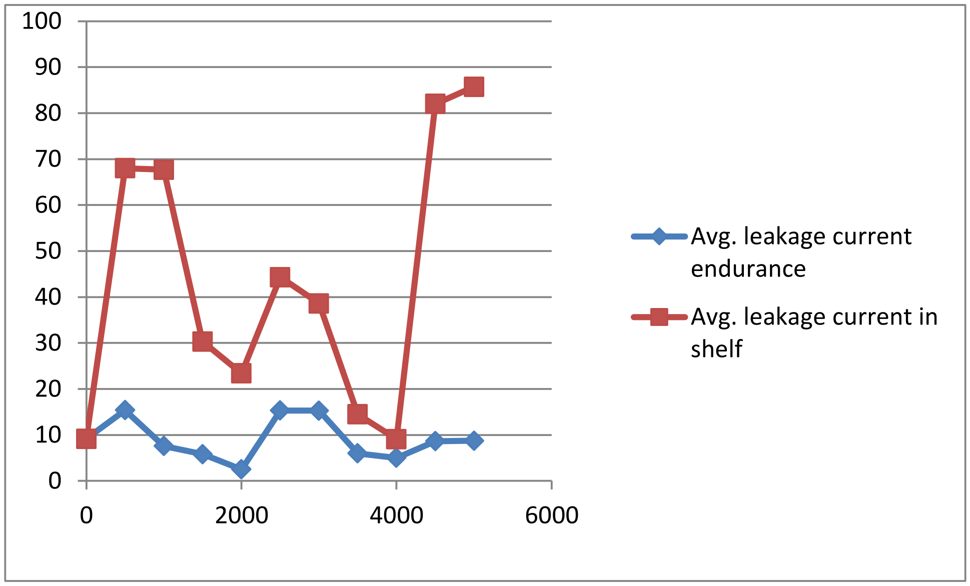


HOURS->

Avg. % Cap. Change Vs Hours



Hours→ **Avg.tan$ Vs hours**



Hours→

Avg. Leakage current Vs Hours

<u>**VARIATION OF IMPEDENCE WITH TEMPERATURE & FREQUENCY (LCV-2)**</u>

DESIGN OF CAPACITOR :

Anode foil :

Cathode foil :

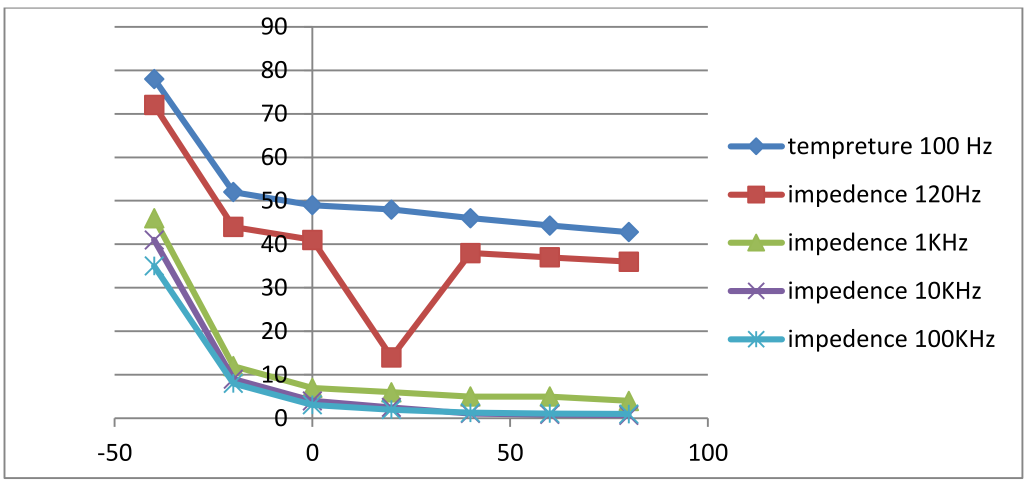
Paper :

Can size : 10*16

Sealing rubber : EPT

Capacitance : 330 uF

Working voltage : 16 volts.



Temperature→

IMPEDENCE VS TEMPERATURE

TEMP.	IMPEDENCE				
C	100Hz	120 Hz	1KHz	10 KHz	100 KHz.
-40	78	72	46	41	35
-20	52	44	12	9	8
0	49	41	7	4	3.1
20	48	14	6	2.5	2
40	46	38	5	1.1	1.3
60	44.3	37	5	0.9	1.1
80	42.8	36	4	0.7	1

Results and Discussion

Two different composition is made with the different combination of solute and solvent. The variation in conductivity of LVC-1 composition with the temperature is slightly higher as compared to LVC-2 composition. It indicate that LVC-2 resultant composition is more stable with regard of temperature. Although recorded pH slightly towards neutral pH and slightly lower spark voltage observed in the case of LVC-1. The no. of trail conducted to examine the composite of capacitor. Experiment show that % change in capacitance is higher in both endurance and shelf test in case of LVC-1. Tan $ property of capacitors is little better, with LVC-1 with almost comparable leakage current property of capacitors with LVC-2.

Similarly Unstability toward temperature may be due to presence of ethylene glycol: Methylene glycol combination with excess water, base in LVC-1 Composition. Although both compositions successfully completed life test of capacitors as per the norms recommended in IEC test for approval of capacitors. Study also show impudence decreases with increase in temperature and increases with decrease of temperature and impedance reduce with increase in frequency.

Electrical parameters of capacitors like percent capacitance change , tan$ and leakage current with temperature at constant frequency i.e.

100Hz are being studied and verify all are the temperature dependent properties of capacitors with the following conclusion.

1. Capacitance decreases with the decrease in expose temperature of components.
2. Tan$ increases with decreasing in temperature in which component is expose.
3. Leakage current increases with increase in temperature.

Analytical Purity of Chemicals and its Analysis

General specifications of chemicals:

	ITEMS	SPECIFICATION
ACIDS	If present as CH3COOH%	0.006 MAX.
WATER	H_2O %	0.21 MAX.
Chloride	Cl %	0.00001 Max.
Sulfate	SO_4 %	0.00051 Max.
Iron	Fe %	0.000021 Max.
Heavy metals	as Pb %	0.0002 Max.
Assay	G.C. Method %	99.0

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