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Effect of Chloride Ion on the Behaviour of Electrolytic Capacitor

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Aluminum electrolytic capacitors up to 100 working volt, contaminated intentionally with chloride ions, through the electrolytic solution were studied. This systematic comparative study was undertaken on the adverse effects of chloride ions on these capacitors, impregnated with 0.4, 0.5, 0.8, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 ppm chloride contaminated electrolyte along with uncontaminated electrolyte. The life test of the capacitors was carried out at 85°C up to 2000 h. For these low voltage capacitors the detrimental effect is negligible up to 50 ppm and no remarkable change is observed compared to the uncontaminated electrolyte. Higher chloride concentration has destructive effect in its life test, even in the manufacturing process due to severe anode corrosion, observed through photomicrograph. All supporting electrical parameters including ESR of these capacitors have been done extensively in the present article.

Key Words: Aluminum electrolytic capacitors, Capacitance, Corrosion.

INTRODUCTION

Aluminum electrolytic capacitor (Elcap) plays a significant role in the electronic circuit with its wide applications from small transistor to high power computers due to its several unique features. The low cost nature per microfarad and per ripple ampere and above all its very high capacitance per unit volume are the notable advantages. However, they present problems in their application field and sometimes even in their manufacturing process. One of the major causes of these problems is the undesirable contamination of chloride ions. The chloride ions are known for their deleterious action in Elcaps, whether present in raw material or electrolyte.

The electrolyte, *i.e.*, carrier of ions has an inherent part in capacitors[1–3], batteries[4–6] and other electrochemical devices. Even very minute contamination inside the capacitor spread by carrier electrolyte can deteriorate the life of the capacitor in its application field. Several researchers have studied globally on the basic structure of Elcaps[7–9] but a detailed study on the effects of aggressive

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chloride ion intrusion in the Elcap is scarce. Corrosion with in Elcap is a congenital problem from its inception in the electronic field, due to unwanted ions, especially chloride ions[10]. The corrosion of aluminum metal with chloride and other ions were studied by previous workers [11-13]. Richardson and Wood [14] attempted to study the behaviour of corrosive and inhibitive effect of different ions on the capacitance and dissipation factor of Elcaps. However, any systematic and thorough study has not been done in this direction so far.

In the present paper, studies have been done to see the effect of concentration of Cl^- on the life of low voltage capacitors, *i.e.*, up to 100 V. An optimization has been worked out for the permissible limit of Cl^- intrusion from the environment or from the raw materials during its manufacturing process, specially in case of low voltage capacitors.

EXPERIMENTAL

Electrolyte: A stock solution of 1000 ppm Cl^- content was prepared by dissolving calculated amount of AR grade NaCl (Glaxo) in the electrolyte (own composition). This was diluted to 0.4, 0.5, 0.8, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 ppm with the same electrolyte and was taken for experimentation. The conductivity and pH were measured by CM-20E and HM-20E TOA Japan respectively.

Materials: Commercially available raw materials, *e.g.*, anode foil, cathode foil, electrolytic paper, terminals, rubber bung and aluminum can etc. are used, some of which after repeated washing with deionized water and drying at 85°C

Construction of capacitors: The anode foil, cathode foil and electrolytic paper were winded up, impregnated (soaked) with the electrolytic by vacuum and sealed inside the aluminum can with the help of rubber bung. The construction procedure is described elsewhere[2–7].

The Elcaps made for this experimentation are given in Table-1. To avoid clumsiness the data have been trimmed and selected data taken for consideration and convenient interpretation.

The ready to use capacitors were kept overnight at room temperature, then measured the capacitance, dissipation factor (DF), equivalent series resistance (ESR) by Hewlett Packard 4274a Multi-frequency LCR meter at 120 Hz frequency. The leakage current was measured after 5 min of charging at working voltage.

Environmental test: The capacitors were kept in uncharged condition for shelf and continuously charged at working voltage for endurance test both at 85 ± 2°C. At regular intervals the parameters were monitored after keeping the elcaps for 12–16 h at normal room temperature. All measurements were done at controlled temperature of 252°C throughout the experiment.

Micrograph: Photomicrographs were taken through Olympus zoom stereomicroscope SZ4045STR attached with PM-10M camera of 10x magnification.

TABLE-1

Capacitance (μF/working volt)	Can size D × L (mm)	Ageing (volt)	Chloride level of electrolytes (ppm)	Chosen concentration for comparison
100/63	10 × 12.5	73	0.4, 0.5, 0.8 and uncontd.	0,8 and uncontd.
220/100	12.5 × 25	115	0.51, 25 and uncontd.	1, 5 and uncontd.
100/100	10 × 20	115	1, 2, 5, 10 and uncontd.	5, 10 and uncontd.
70/40	10 × 20	46	10, 20, 40, 500 and uncontd.	10, 50 and uncontd.
220/100	12.5 × 25	115	100, 200, 500 and uncontd.	100 and uncontd.
47/63	10 × 12.5	73	10, 50, 100 and uncontd.	10, 50, 100 and uncontd.
470/35	12.5 × 21	41	1000 and uncontd.	1000 and uncontd.

RESULTS AND DISCUSSION

Electrolyte used was polyesteric in nature[7–16] and known for its conventional use in electrolytic capacitors. Electrolyte contaminated with additional Cl^- ions cannot contribute much to the conductivity of the solution due to the dissolved solutes of the electrolyte itself. This is imperative from the results of Table-2 and virtually no gradation of the parameters is observed. The spark voltage[15], *i.e.*, the basic parameter for selection of an electrolyte is not also effected by the Cl^- intrusion.

TABLE-2
CHARACTERISTICS OF ELECTROLYTES

Electrolyte	pH	Conductivity (S/cm) × 1000
Electrolyte—Uncontaminated	6.23	6.42
Electrolyte with 1 ppm Cl^-	6.22	6.37
Electrolyte with 10 ppm Cl^-	6.20	6.22
Electrolyte with 100 ppm Cl^-	6.17	6.29
Electrolyte with 1000 ppm Cl^-	6.20	6.40

From the initial observation of capacitance, dissipation factor (DF) and leakage current (LC), the capacitors have the same values whether contaminated or uncontaminated up to 50 ppm Cl^- ions.

The capacitors under shelf life test are having similar values for capacitance, D F independent of chloride instruction. However, in this test, the capacitance is less and LC is more compared to the capacitors under endurance test except the initial values, observable from Table-3. Sparing dissolution of the dielectric oxide layer increases the LC and the deposition of $Al(OH)_3$ as a result of reaction of anode foil with aqueous electrolyte, causing to reduce the capacitance of anode plate at the shelf life test at uncharged condition. Ultimately, both the factors cause a slight reduction of DF compared to endurance values. Yet, the capacitors under shelf life test do not have any conclusive effect regarding Cl^- intrusion.

TABLE-3
COMPARISON OF PARAMETERS OF CAPACITORS 47 μF/6 3V UP TO 100 h IN SHELF AND ENDURANCE TEST WITH SELECTED CONCENTRATION OF Cl^- CONTAMINATION

Electrolyte	Parameters	Initial		500 h		1000 h	
		End	Shelf	End	Shelf	End	Shelf
Uncontd.	Cap in μF	45.30	45.50	45.60	44.87	45.20	44.92
	DF in %	4.15	3.66	4.20	3.24	4.58	3.34
	ESR in ohm	1.21	1.07	1.22	0.6	1.34	0.99
	LC in μA	10.40	1.35	1.35	3.04	0.52	22.15
10 ppm	Cap in μF	45.50	45.53	45.90	44.53	44.50	44.60
	DF in %	3.97	3.93	4.28	3.52	4.51	3.62
	ESR in ohm	1.15	1.14	1.23	1.05	1.31	1.08
	LC in μA	10.30	12.90	0.85	22.66	0.54	31.87
50 ppm	Cap in μF	45.10	44.80	45.20	44.60	44.40	44.69
	DF in %	4.24	4.53	4.60	3.66	5.15	3.67
	ESR in ohm	1.25	1.35	1.34	1.09	1.53	1.09
	LC in μA	12.30	12.90	0.88	22.56	0.51	31.90
100 ppm	Cap in μF	44.70	44.56	45.30	45.69	45.00	45.55
	DF in %	4.58	4.07	4.27	3.56	4.78	3.54
	ESR in ohm	1.36	1.16	1.25	1.03	1.41	1.03
	LC in μA	36.40	37.90	1.55	30.50	1.53	23.02

100/63 and 220/100 μF/V capacitors crossed 3000, 2500 h respectively unabated with electrolyte contaminated up to 5 ppm. The deterioration of the dielectric layer due to Cl^- ions of concentration up to 50 ppm is less, *i.e.*, the rate of deterioration is less compared to the rate of formation of Al_2O_3 on the anode foil during ageing or endurance test.

Initial LC value for the capacitors with 100 ppm contaminated electrolyte is high compared to uncontaminated for all capacitors like 220/100, 470/63, 47/63 μF/V etc.

However, the capacitors recover the LC after endurance test of 85°C at working voltage. Here also deterioration rate is slow; conversely, healing up rate of oxide film is fast. Furthermore, the deterioration of the Elcap at endurance test is fast at the high temperature of 105°C. In spite of stable LC value after 192 h, Elcaps of 220 μF/100 V have lasted for 1000 h during endurance at 85°C and finally busted with shortage of electrodes. However, Elcaps with less capacitance and low working voltage show a proportionate increase of life in endurance test, observed from Table-4. Analysis of discarded capacitor (220/100) showed unaffected edges of the anode foil and corroded terminals, similar to photomicrograph for 200 and 500 ppm.

While at the opposite end, the effect of Cl^- contamination is pronounced in expectation with highest chloride concentration. Capacitors having electrolyte with 1000 ppm were aged with difficulty and current became 50 mA per capacitor at 65°C during ageing. These became bulged at hot ageing and opening of the piece for failure analysis indicating the corrosion of anode foil. From the photo micrograph, it was observed that the edges of the anode foil became corroded throughout the foil with a grayish to black deposition on the terminal possibly due to $AlCl_3$ deposition or similar side products. The edges of anode foil and junction of the terminal and foil, desirous of Al_2O_3 coating, became eroded causing high flow of current and consequently high LC. The insulating oxide layer of these two portions was depleted due to corrosion by chlorine on Al/Al_2O_3, generated during electrolysis of aqueous electrolyte at ageing.

Similarly, anode erosion is observed also with electrolytes contaminated in between 100 and 1000 ppm. Erosion is less up to 200 ppm but more for 500 ppm Cl^- contaminated electrolyte. Causes of corrosion with these electrolytes are same as that of 1000 ppm; however, severity of anode erosion is limited around the terminal only. The edges of the anode foil in both the cases remain unaffected. At the high temperature of 105°C the endurance life of the capacitors (470 μF/ 63 V) with 200 ppm reduced to half compared to 48 h at 85°C . Both high temperature and charge increase the rate of corrosion. In the absence of charge at shelf life test, these elcaps (220/100) behave normally like uncontaminated capacitors. In most cases, corrosion around terminal is attributed by the current density at the time of ageing or endurance test.

An analogy has been drawn for the premature failure of the capacitors in Table-4.

Conclusion

The chloride ions electrochemically react with aluminum or aluminum oxide much faster than the normal course of chemical reaction. Up to a certain level of Cl^- contamination, the corrosion is much less even after application of working voltage to the Elcaps. Capacitors with 50 ppm Cl^- intrusion behave normally up to 200 h at working voltage of 63 V at 85°C. Hence preferential oxidation is suggested for aluminum up to this level by virtual electrolysis within the capacitor. Chloride ions cannot be liberated or interfere to erode the aluminum oxide at this stage. Beyond this, the Cl^- ions affect the Elcap abruptly and drastic change occurs during or after its preparation. This study further suggested to scrutinize the permissible limit of Cl^- for aluminum capacitor.

TABLE-4
SUMMARY OF BEHAVIOUR OF CAPACITORS WITH ELECTROLYTE, CONTAMINATED HIGHLY BY Cl^- IONS

Contamination (ppm)	Capacitors made (μF/volt)	Effect
100	220/100	LC is a little high initially. However, completed 100 h at 85°C in endurance test. No physical deformation. Corrosion at terminal only.
	470/63	Same as above but failed within 1250 h at 85°C and 500 h at 105°C respectively in endurance test.
	47/63	Completed 200 h unabated in endurance test.
200	220/100	LC is high. Failed within 48 h at 85°C in endurance test. Bulging during endurance test. Corrosion on terminal only.
	470/63	Same as above but failed with in 24 h in endurance test of 105°C.
500	220/100	Little bulging during ageing. Abnormally high LC. Unfit for life test. Corrosion around the terminal only.
	470/63	Same as above
1000	470/35	The process of ageing is very slow and current flow is high at room temperature. Difficulty in ageing at higher temperature. LC is enormously high. Capacitors became bulged during ageing and unsuitable for life test and terminal revealed in the photomicrograph.

REFERENCES

1. C.J. Kaiser, The Capacitor Handbook, Van Nostrand Reinhold, KCSJ, p. 51 (1990).
2. F.J. Burger and L. Young, in: J.B. Briks and J. Hert (Eds.), Progress in Dielectrics, Vol. 5, Academic Press, New York, p. 1 (1963).
3. J.P. Zheng and T.R. Jow, *J. Electrochem. Soc.*, **144**, 2417 (1997).
4. D.A.J. Rand, K. Fucjida, W.F. Gillman, D.W.H. Lambert and J.E. Manders, *J. Power Sources*, **38**, 197 (1992).
5. A.P. Chattaraj and I.N. Basumallick, *J. Power Sources,* **36**, 557 (1991); *J. Power Sources,* **55**, 123 (1995).
6. ————, *J. Power Sources,* **37**, 411 (1992).
7. R.S. Alwitt and R.G. Hills, *IEEE Transactions*, **28** (Sept. 1965).
8. R.S. Alwitt, *J. Electrochem. Soc.*, **116**, 1024 (1969).
9. J.S. Shaffer, M.R. Arora and J.L. Stevens, *Powertronics*, **1**, 14 (1985).
10. G. Burri, W. Luedi and O. Haas, *J. Electrochem. Soc.*, 136, 2167 (1989).
11. A. Goldman and R. Sigmond, *J. Electrochem. Soc.*, **132**, 2842 (1985).
12. K.P. Wong and R.C. Alikre, *J. Electrochem. Soc.*, **137**, 2842 (1990).
13. J.R. Davis, ASM Speciality Handbook on Aluminum and Aluminum Alloys, ASM International, The Materials Information Society, p. 579 (1994).
14. J.A. Richardson and G.C. Wood, *J.Electrochem. Soc.*, **12**, 193 (1973).
15. F.J. Burger and J.C. Wu, *J. Electrochem. Soc.*, **118**, 2039 (1971).
16. I.L. Finar, Oraganic Chemistry, Vol. I, ELBS & Longman, p. 450 (1982).

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