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NEW HIGH PERFORMANCE ALUMINUM ELECTROLYTIC CAPACITORS

by

F. J. BURGER and D. M. CHESELDINE
Sprague-TCC (Canada) Ltd.
Toronto, Ontario, Canada

and

J. A. MORESI
Sprague Electric Company
North Adams, Mass.

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SPRAGUE ELECTRIC COMPANY
North Adams, Massachusetts

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SUMMARY

The shortcomings of conventional aluminum electrolytic capacitors are discussed, in particular their lack of stability and limited temperature range.

A new type of aluminum electrolytic capacitor is described of high stability and an operating temperature range from -55 C to +125 C.

It owes its superior performance characteristics to the development of a new electrolyte system representing a complete departure from the customary glycol/borate electrolytes.

Typically, the impedance increases by a factor of about 1.2 when going from +25 C to -55 C and extended life and shelf tests at 125 C show an exceptional stability of the electrical parameters comparable with or surpassing those of tantalum foil capacitors.

INTRODUCTION

The new types of aluminum electrolytic capacitors to be described were developed under a Canadian Government Sponsored Research and Development Project. After feasibility had been established, the work was continued with substantial company support.

It is not the purpose of this paper to give extensive performance data or list in detail physical sizes of every available capacitor unit (because such data have been published elsewhere) but rather to describe the development and to discuss some of the guide lines which were followed in this work.

Up to very recently, the field of commercially available aluminum electrolytics presented certain features of stagnation. There is at present no lack of variety in types, sizes and ratings, but working temperature range and electrical performance have been virtually unchanged for a considerable period. In spite of some considerable patent activity in the field of electrolytes for electrolytic capacitors in general, many manufacturers still do not feel any real need for departing from the ethylene glycol/borate system that had been so well established. The reason for this conservatism is that ethylene glycol/borate systems are very safe chemically and are entirely compatible with the anodic aluminum oxide dielectric and all the other materials employed in the construction of the component.

There are, however, many shortcomings of the glycol/borate system that limit severely the conditions under which aluminum capacitors will operate satisfactorily. For instance, the large change of electrolyte resistivity with temperature (typically this may be about 4% per °C at temperatures near 25C) causes large increases in the impedance of capacitors at low temperatures thereby restricting their lower operating range to about -40C. Hence, aluminum capacitors containing conventional electrolyte systems as mentioned suffer from the twin disadvantages of too restricted a temperature range and too large a change of electrical performance characteristics within this limited range.

This becomes apparent by reference to two important Military specifications, one covering aluminum capacitors[1], the other tantalum capacitors[2]. With due allowance made for a time lag, these two specifications afford a good illustration of the current capabilities of the industry.

For instance, the temperature range covered by the tantalum foil capacitor specification is from -55C to +125C whereas that of the aluminum foil capacitors is from -40C to +85C, i.e. narrower by 55C.

Permitted impedance increases, when proceeding from room temperature to the specified low temperature, range from about 5- to 15-fold, at -40C, for aluminum electrolytics, but only from 2- to 5-fold, at -55C, for tantalum foil capacitors, according to the two cited specifications. Largely as a result of the work reported here, it has become feasible to draft a specification for aluminum electrolytic capacitors[3] having an operating temperature range from -55C to +125C. Impedance increases permitted by this new specification when proceeding from room temperature to -55C are from 1.5-fold to 3-fold, i.e. actually less than what is currently permitted for the comparable type of tantalum foil capacitors.

Before describing other properties of the new capacitors we would like to discuss the more important factors that have made the development possible.

NEW ELECTROLYTE SYSTEMS

The key factor is a new electrolyte system.[4, 5]

The ethylene glycol/ammonium-borate based electrolytes show large increases of viscosity and hence resistivity with decreasing temperature. Some of the formulations are not just simple solutions of ammonium pentaborate in ethylene glycol, but rather complex equilibrium mixtures of polyesters of boric acid and ethylene glycol. Esterification and condensation reactions may and do continue during the service life of the capacitor with resulting loss of water at higher operating temperatures.

Owing to the presence of a considerable amount of hydroxyl in the unreacted ethylene glycol and the presence of large molecules as represented by the polyesters of boric acid there is strong molecular interaction between the constituents of any of these electrolyte systems, whether of the reacted or the unreacted type, at lower temperatures.

Further shortcomings of the system are evident at high temperature. Above about 85C, the electrical parameters of many of the capacitors containing glycol/borate electrolytes become unstable, the usual trend being an increase in capacity and dissipation factor, often accompanied by large pressure increases within the container leading eventually to escape of electrolyte. This instability at high temperatures may depend upon the concentration of water in the electrolyte, the latter to be relatively high in cases where low temperature operation is required in order to maintain a reasonably fluid electrolyte.

It is useful when considering alternative electrolyte systems to list certain features that would be desirable for such systems, having due regard to the inadequacies of the glycol/borate electrolytes. Included would be the following:

1. The solvent, in addition to being highly polar and having good solvent power for ionogens, should be chosen such as to result in a minimum temperature coefficient of conductance of the electrolyte.

2. The electrolyte should contain very little water.

3. Hydration of the anodic oxide should, preferably, be inhibited by taking special measures, since total elimination of water from the electrolyte is impracticable, it being present anyway, though in a combined state in the cellulose spacer of the capacitor and in certain anion species which are normal constituents of a capacitor electrolyte.

4. The resistivity should be low and adjustable by means other than by varying the water content.

5. The electrolyte must be capable of forming the oxide film under anodizing conditions without permitting the occurrence of undesirable side reactions.

Further, obvious considerations are that the electrolyte should remain liquid over the operating temperature range of the capacitor and that it should not corrode or attack any of the parts of the capacitor with which it comes into contact.

With tantalum foil capacitors, manufacturers found it possible to depart from the electrolyte system that was, and still is preferred for aluminum electrolytic capacitors at large. Owing to the fact that tantalum metal and its oxide are much more resistant to corrosion than aluminum and its oxide, there is considerably more latitude in the choice of electrolytes for tantalum capacitors. As a result, several families of electrolytes based on dimethyl formamide were developed at the Sprague Electric Company[6] and have been largely adopted by the industry.

It was therefore natural to consider dimethyl formamide as one of the possible solvent constituents for aluminum electrolytic capacitors. Besides being an excellent solvent for many solutes, dimethyl formamide has a very flat viscosity temperature characteristic and a wide liquidus range. It is also essentially non-reactive: in particular, it does not enter into esterification or polymerisation reactions, under conditions that occur during the working life of the capacitor. As a result, DMF based electrolytes show more stable resistivity/temperature and resistivity/time characteristics than do ethylene glycol based systems.

It became, however, apparent very quickly after commencement of our study that any approach towards devising an effective electrolyte system for extended temperature aluminum electrolytic capacitors had to be much more subtle than being simply a substitution of one solvent (ethylene glycol) for another (DMF).

It was necessary to analyze the different functions that had to be performed by an efficient capacitor electrolyte and to devise specific means to achieve capability in those functions.

Among the problems encountered that had to be solved were the following:

One was that the solvent had only a limited solubility for certain desirable ionogens such as ammonium borate or boric acid. This difficulty was overcome by using mixed solvents, the major component being DMF, minor constituents being lower molecular weight polyhydric alcohols and ethers of such alcohols, and by using alkylated ammonium borates which were more soluble than ammonium borate itself.

Another problem relates to conductivity. In order to achieve high conductivity in the electrolyte, highly soluble and dissociable salts such as formates were added, in addition to those primarily chosen for their good forming properties e.g. borates, which have been mentioned frequently and obviously occupy a position of prominence in aluminum electrolytic capacitors for reasons that are by no means clear.

A third problem is concerned with chemical stability of the anodic oxide. The barrier properties of aluminum oxide films are destroyed by prolonged contact with water, particularly at temperatures above about 85C. The desirability of making additions to the electrolyte system which would inhibit this destruction was mentioned previously. A series of experiments in which ammonium phosphate was added to glycol based electrolytes which contained some water showed this additive to be highly effective. Foils on which anodic oxide had been formed and others covered only with the naturally occurring air oxide both showed large capacitance increases when immersed in electrolyte at 125C for prolonged periods, whereas the addition to the electrolyte of as little as 0.01% $NH_4H_2PO_4$ drastically reduced and sometimes reversed these changes.

A major problem was encountered during early phases of the project, namely the observation of a corrosive attack on the capacitor anode.

Though at first appearing to be fundamental to the non-aqueous nature of the electrolyte formulation, it fortunately did not prove to be so. It was solved by adding to the electrolyte specific inhibitors in quite low concentrations.

As a result of this development work, a system of aluminum capacitor electrolytes was evolved of a sufficiently broad conductivity spectrum to cover a variety of rated voltages ranging from 5 to 300 volts, with a promise of higher voltages. By varying the concentration of solute and by selecting the proper solvent mixture the electrical resistivity for each of the ratings required can be easily optimized, the range covered being 100 ohm-cm to about 800 ohm-cm.

SOME CONSTRUCTIONAL DETAILS

Having devised the new electrolyte system, it became necessary to attend to certain dependent matters.

The first is a consequence of the relatively low value of the resistivity/temperature variations of the new electrolyte system.

For example, at -55C, the resistivity of the new electrolytes is from ten to twenty times that of room temperature. The corresponding factor for some glycol based electrolytes is several hundred. Hence, it becomes possible now to utilize to much better advantage than before aluminum foils with considerably improved "gain". Such foils have become available recently. (The "gain", by definition, is the ratio of the capacitance of etched foil to the capacitance of plain foil of the same projected foil area, both foils formed to the same voltage). By using very high gain foil and, furthermore, by having only one seal in the polar, single ended, version of the new capacitors, it has been possible in many cases to get more capacitance into a given volume, at a given voltage, than can be done with etched tantalum foil.

Another major problem that had to be solved concerns the seal of the new capacitors.

DMF being a very active solvent, it attacks many of the materials which are customarily used for capacitor seals. Among the materials found best to resist the action of DMF are polytetrafluoroethylene, polypropylene, and certain butyl rubber formulations. All of these are being used at present.

After considerable development work, a PTFE seal with butyl rubber gasket and metal parts consisting of aluminum and solderable leads was evolved, as illustrated in Figure 1. Connections to the capacitor element are by welding.

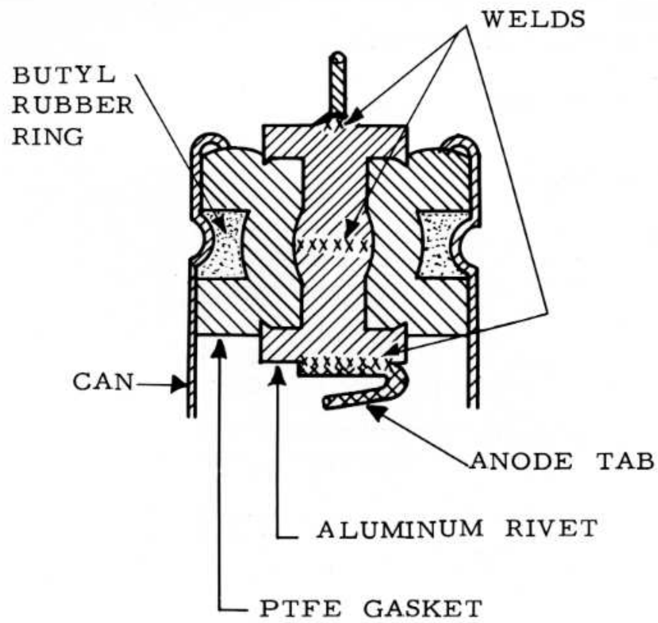

Figure 1

END-SEAL FOR TUBULAR CAPACITOR

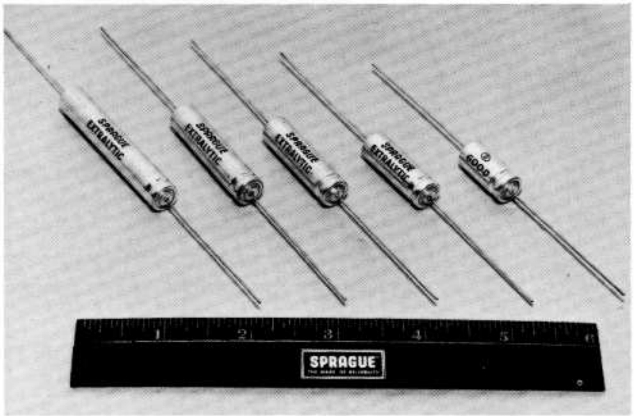

Figure 2B

POLARIZED ALUMINUM ELECTROLYTIC CAPACITORS

In Figure 2 are shown units of one of the families of capacitors that are being produced as a result of the work described.

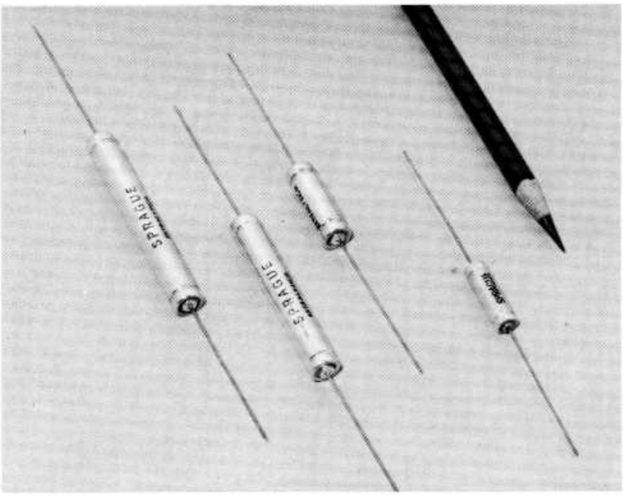

Figure 2A

NON-POLARIZED ALUMINUM ELECTROLYTIC CAPACITORS

PERFORMANCE CHARACTERISTICS

Below we present a very condensed summary of test results of some ratings, polar and nonpolar, including life and shelf tests. Some of the results were obtained with ratings which in performance and physical size are exact replacements of existing MIL-C-3965C tantalum foil capacitors.

Capacitors rated from 10V to 150V, both polar and nonpolar styles, were tested by CAMESA (Canadian Military Electronic Standards Agency) to MIL-C-3965C, detail sheets 17B and 18B, i.e. those applying to 125C etched tantalum foil tubular capacitors. The results showed the new capacitors to comply fully with that specification. This is illustrated in Tables I and II.

Table I gives a summary of temperature stability tests. Also indicated are limits according to the appropriate detail sheets of the tantalum capacitor specification MIL-C-3965C as well as the limits that have been proposed for the new extended temperature range aluminum oxide capacitor specification MIL-C-39018. It will be seen that the capacitors reported on are well within the limits of either of the two specifications.

Table II gives a summary of 1000 hour and 2000 hour life test results, (also carried out by CAMESA) showing full compliance with the requirements of the two specifications named.

TABLE I
HIGH PERFORMANCE ALUMINUM ELECTROLYTICS
RESULTS OF
TEMPERATURE STABILITY TESTS

RATINGS		TEMPERATURE °C					
		+25		-55		+125	
POLAR		Lkge	D.F.	Δ C	Z Ratio	Lkge	Δ C
VOLTS	µF	µA	%	%	Z-55/Z+25	µA	+%
10	400	0.8	3.7	10	1.17	11	20
30	100	0.5	2.1	7	1.15	13	7
50	70	0.6	1.3	7	1.10	15	6
100	25	0.6	2.2	8	1.09	6	12
150	17	0.6	3.2	9	1.10	6	10
MAX. LIMITS (SEE NOTE)							
MIL-C-3965/17B		4.0	15	35	2.6	75	30
MIL-C39018 (Draft)		7.0	10	30	2.2	20	25
NON-POLAR		Lkge	D.F.	Δ C	Z Ratio	Lkge	Δ C
VOLTS	µF	µA	%	-%	Z-55/Z+25	µA	+%
10	250	0.3	3.2	12	1.10	4	20
30	60	0.3	2.4	8	1.26	3	7
50	35	0.8	2.1	8	1.16	2	7
100	12	0.2	3.2	11	1.13	2	13
150	8	0.2	2.6	8	1.10	4	11
MAX. LIMITS (See Note)							
MIL-C-3965/18B		4.0	15	40	2.2	75	30
MIL-C39018 (Draft)		7.0	10	30	1.5	20	25

NOTE: Limits shown are the most stringent ones listed in the appropriate detail sheet for case size D4 (Diameter: .375": Length: 2.156")

TABLE II

HIGH PERFORMANCE ALUMINUM ELECTROLYTICS
RESULTS OF LIFE TESTS AT 125°C

RATINGS		LIFE TEST HOURS, AT 125°C AND RATED VOLTAGE						
		1000	2000	1000	2000	0	1000	2000
POLAR		LEAKAGE		Δ C		D. F.		
VOLTS	µF	µA	µA	-%	-%	%	%	%
10	400	0.5	0.5	2.6	3.3	4.2	4.4	4.3
30	100	0.3	0.2	1.0	0	1.9	2.1	2.0
50	70	0.1	0.1	0	1.4	1.3	1.6	1.6
100	25	0.1	0.1	1.1	1.1	2.2	2.4	2.3
150	17	0.2	0.1	0	0.6	4.4	4.1	3.6
MAX. LIMITS								
MIL-C-3965/17B		-	4.0	-	15	15	-	15
MIL-C-39018 (Draft		-	7.0	-	15	10	-	10
NON-POLAR		LEAKAGE		Δ C		D.F.		
VOLTS	µF	µA	µA	-%	-%	%	%	%
10	250	0.6	0.2	2.0	2.4	3.2	3.8	3.6
30	60	0.5	0.2	1.6	1.6	2.3	3.2	2.9
50	35	0.5	0.4	0.9	1.1	2.0	2.4	2.2
100	12	0.5	0.5	0	0	2.9	2.8	3.0
150	8	0.9	0.1	1.2	1.2	2.9	3.3	3.3
MAX. LIMITS								
MIL-C-3965/18B		-	4.0	-	15	15	-	15
MIL-C-39018(Draft)		-	7.0	-	15	10	-	10

TABLE III

HIGH PERFORMANCE ALUMINUM ELECTROLYTICS

RESULTS OF SHELF TEST, AT 125°C

RATINGS		SHELF TEST HOURS, AT 125° C							
		0	1000	2000	1000	2000	0	1000	2000
POLAR		Leakage			ΔC		D.F.		
VOLTS	µF	µA	µA	µA	-%	-%	%	%	%
10	400	0.3	4.9	6.0	4.9	6.3	4.6	5.0	4.6
30	100	1.6	3.2	4.4	1.5	2.1	3.0	2.8	3.2
50	70	0.6	3.1	3.9	2.8	3.4	1.4	1.4	1.3
100	25	0.6	4.4	4.7	2.3	2.6	2.3	2.0	2.0
150	17	0.6	2.5	3.7	1.9	2.2	3.9	3.4	3.6
MAX. PROPOSED LIMITS (AFTER 500 HRS.)									
MIL-C-39018 (Draft)			14		±10%		10		
NON-POLAR			Leakage		ΔC		D.F.		
VOLTS	µF	µA	µA	µA	-%	-%	%	%	%
10	250	0.3	3.2	6.0	1.8	2.3	3.5	3.6	3.8
30	60	0.3	2.4	3.5	0.8	1.3	3.1	2.8	3.4
50	35	0.5	3.6	6.0	1.0	1.5	2.1	1.8	1.8
100	12	0.1	2.3	3.6	1.1	1.3	3.5	2.7	3.6
150	8	1.3	9.5	7.5	0.1	0.5	3.0	2.9	3.3
MAX. PROPOSED LIMITS (AFTER 500 HRS)									
MIL-C-39018 (Draft)			14		±10%		10		

TABLE IV

HIGH PERFORMANCE ALUMINUM ELECTROLYTICS

RESULTS OF LONG TERM LIFE TESTS

POLAR RATINGS		LIFE TEST HOURS, at 125° C AND RATED VOLTAGE						
VOLTS	µF	4000	8000	4000	8000	0	4000	8000
		Leakage µA		ΔC %		D.F. %		
30	100	0.5	0.5	+5.3	+1.8	3.5	5.3	5.7
50	70	0.2	0.2	+3.1	+2.8	2.3	3.3	3.5
150	17	0.2	0.3	-0.5	-1.0	2.4	6.4	7.2

TABLE V

HIGH PERFORMANCE ALUMINUM ELECTROLYTICS

RESULTS OF LONG TERM SHELF TESTS

POLAR RATINGS		SHELF TEST HOURS, AT 125°C					
		0	4000	4000	0	4000	
VOLTS	µF	Leakage µA		ΔC%	D.F. %		
10	400	0.7	9.0	-8.8	8.2	6.5	NOTE 1
150	17	0.5	25	-5.2	3.2	6.1	NOTE 2

POLAR RATINGS		SHELF TEST HOURS, AT 25°C					
		0	24000	24000	0	24000	
VOLTS	µF	Leakage µA		ΔC%	D.F. %		
5	140	3.0	2.2	0.6	3.7	3.1	
20	40	2.5	1.9	0.8	2.2	2.1	NOTE
100	10	5.8	7.2	0.2	3.2	3.0	3

NOTE 1: Leakage was measured at 15V) Units were
NOTE 2: Leakage was measured at 200V) dual-rated
NOTE 3: Zero hour reading was taken following a 500 hour Shelf Test at 125°C

In Table III, Shelf Test results, at 125C, obtained in our own laboratories, are summarized.

The Shelf Test is not a requirement of the tantalum foil capacitor specification. However, it may be useful, at the present time, to include such a test in the new specification, as has indeed been proposed, in order to allay any doubts that may exist about the performance capabilities of the new capacitors.

The duration of the test presently proposed is 500 hours. It will be seen from Tables III, IV and V, that degradation of these capacitors, even over very prolonged periods, is very small indeed.

Extensive reliability data are still being accumulated, but all available information strongly encourages the belief that the new aluminum capacitors represent a group of components of high reliability.

REFERENCES

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2. MIL-C-3965C, Military Specification, Capacitors, Fixed, Non-Solid Electrolytic (Tantalum Foil & Sintered Slug), General Specification for, 6 March 1963.
3. MIL-C-39018, (Proposed) Military Specification, Capacitors, Fixed, Electrolytic (Aluminum Oxide), General Specification for. Initial Draft, 29 May 1964.
4. Canadian Patent 694253, F.J.P.J. Burger & D. M. Cheseldine, to Canadian Government Sept. 15, 1964.
5. Canadian Patent 694909, F.J.P.J. Burger & D. M. Cheseldine, to Canadian Government Sept. 22, 1964.
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