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**PROGRESS REPORT**

SIXTH QUARTER  
JANUARY 1964

**ELECTROLYTIC NIOBIUM  
AND  
NIOBIUM ALLOY CAPACITORS**

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RESEARCH AND DEVELOPMENT WORK  
ON ELECTROLYTIC NIOBIUM AND NIOBIUM ALLOY CAPACITORS  
OF WET AND SOLID TYPES

BUREAU OF SHIPS CONTRACT Nobsr-87478

SIXTH QUARTERLY PROGRESS REPORT

OCTOBER 1, 1963 - DECEMBER 31, 1963

ELECTROLYTIC NIOBIUM AND NIOBIUM ALLOY CAPACITORS

OF WET AND SOLID TYPES

BUREAU OF SHIPS CODE 691A2

SUBJECT:

Bureau of Ships Contract NObsr-87478  
Quarterly Research and Development Report, October 1, 1963 - December 31, 1963,  
and Final Engineering Report.

REFERENCE

Project Serial No. SR-0080302 ST 9600

PROGRAM OBJECTIVES

The development of 35, 50 and 100 volt niobium electrolytic capacitors of highest possible capacitance values, capable of full voltage operation at 85°C and with design objectives as listed in Military Specification MIL-C.26655 for:

- (1) electrical parameters,
- (2) environmental characteristics,
- (3) spatial configuration and dimensions,
- (4) operating temperature range (-65°C to +85°C).

Report written by:

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## SECTION I - SIXTH QUARTERLY REPORT

### Task A - Work on Niobium and Niobium Alloy Sintered Anode Capacitors of Wet and Solid Electrolyte Types

#### SUMMARY OF PROGRESS

##### Activity 5 - Determination of Optimum Processing Conditions for Niobium Porous Anode Solid Electrolyte Capacitors

###### A. Objective

The object of this work is to determine the best processing methods for the preparation of niobium porous anode solid electrolyte capacitors up to the canning stage. Parameters to be studied in this phase include optimum particle shape and size distribution, green density of anodes, sintering conditions, chemical etching and reformation-impregnation conditions.

###### B. Results of Recent Studies

###### (a) Sub-Activity 5.3 - Determination of Optimum Particle Size Distribution for Niobium Powders Used in Pressing Capacitor Anodes

###### Powder Agglomeration Studies

In previous reports, some evidence was described indicating that increased capacitance (as measured by two parameters, charge number  $A$  and size factor  $S$ ) is obtainable by use of progressively smaller niobium powder particle sizes to press anodes, until a maximum size factor is reached at a geometric mean size of ten microns. However, a rapid increase in dissipation factor at 1000 cps was also found to occur with decreasing particle size.

An attempt has been made to achieve the increased size factor without the concomitant rise in dissipation factor, by agglomeration of fine powders. It was hoped in this way to obtain a powder consisting of relatively coarse clinker-like particles with holes in them, and with pressing characteristics that would result in anodes with a large, relatively open, internal pore surface area.

Rectangular slabs, pressed from fine -400 mesh niobium powders, were agglomerated by vacuum sintering at a series of temperatures ranging from 1200°C to 2200°C. The sintered compacts were reduced to relatively coarse -170/+325 mesh powders (88 - 44 microns), and pressed into 0.160" diameter x 0.300" long anodes which were then sintered at 2100°C. Small samples of each powder were also examined at different magnifications in a metallograph, in order to detect possible modifications in particle structure. No striking differences were observed in the structures of powders processed from the slabs agglomerated at different temperatures.

The processing details and results of wet electrical and porosimeter evaluations are given in Tables 1, 2 and 3. On the basis of wet test measurements, no improvement in size factor or dissipation factor was achieved over those obtained with the standard powder blends described in previous reports. In general, the 2200°C agglomeration yields the poorest results, while the 1200°C agglomeration provides anodes with a somewhat higher size factor. In addition, the porosimeter evaluation of Table 3 suggests that the relatively large pore sizes obtained by agglomeration at this low temperature might lead to lower dissipation factors in completed solid capacitors. Although this possibility should eventually be followed up, no further work has been done to date.

(b) Sub-Activity 5.5 - Determination of Optimum Impregnation and Reformation Methods

(1) Chemical Impregnation of Porous Anodes with MnO<sub>2</sub>

Previous studies of thermal damage of the Nb<sub>2</sub>O<sub>5</sub> dielectric layer incurred during conversion of Mn(NO<sub>3</sub>)<sub>2</sub> to MnO<sub>2</sub>, by pyrolysis at temperatures in excess of 250°C, indicated that some alleviation of the problem would result from use of a chemical impregnation process requiring a maximum curing temperature of about 200°C. Of the many possible chemical reactions available for producing MnO<sub>2</sub> at relatively low temperatures, preliminary experiments indicated that the oxidation-reduction between permanganate and manganous ions offered the greatest promise of yielding an MnO<sub>2</sub> impregnant coating with electrical characteristics at least as good as those provided by the conventional thermal conversion of Mn(NO<sub>3</sub>)<sub>2</sub>.

Niobium powder from Material Lot 402 (see Table 5 of Fifth Quarterly Report for description) was selected for this investigation. After water sedimentation treatment to remove powder particles of less than one micron diameter, two powder blends were prepared at different times, both consisting of 25% -200/+325 and 75% -325 mesh size particles. Capacitor anodes of 0.160" diameter and 0.300" length were pressed to a green density of 5.2 gms/cc and sintered at 2100°C for thirty minutes in a high vacuum furnace. After cooling, the vacuum chamber was filled with argon gas and the sintered anodes removed and stored in demineralized water in closed polyethylene containers.

Capacitor anodes were formed to 200 volts for four hours at a current density of 25 ma/gm in Y<sub>1</sub> electrolyte, which was maintained at 25°C by means of a water-dry ice cooling bath.

After washing, formed anodes were impregnated with MnO<sub>2</sub>, either by the standard pyrolytic method [Mn(NO<sub>3</sub>)<sub>2</sub> solution at 50°C with a specific gravity of 1.65 at 16°C, pyrolysis temperature 275°C, standard 4/4 dip-reformation sequence] or by the chemical impregnation method described as follows:

- (a) dipped into sodium permanganate solution and dried at 200°C,
- (b) dipped into manganous nitrate solution and dried at 200°C,
- (c) steps (a) and (b) repeated the desired number of times,
- (d) after the last dipping cycle, anodes dipped once more into manganous nitrate solution and dried at 200°C.
- (e) washed for one hour in three changes of boiling demineralized water,
- (f) heated for thirty minutes at 200°C,
- (g) reformed in the standard manner, washed and impregnated again as in steps (a) through (f),
- (h) reformed a second time in the standard manner.

The concentration of solutions used in this process were:

- (a) 12.4 grams of  $\text{NaMnO}_4 \cdot 3\text{H}_2\text{O}$  per 100 ml of solution or per 200 ml of solution, as noted in Table 4,
- (b) 147 grams of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  per 100 ml of solution.

The following variables in process parameters were investigated:

- (1) dip-reformation sequences of 3/2 (i.e., 3 dips, first reformation, 2 dips, second reformation) 4/3, and 4/4,
- (2) different dipping times in both the  $\text{NaMnO}_4$  and  $\text{Mn}(\text{NO}_3)_2$  solutions,
- (3) different drying times at 200°C,
- (4) two different concentrations of  $\text{NaMnO}_4$  solution,
- (5) standard 0.01%  $\text{H}_3\text{PO}_4$  reformation electrolyte versus special reformation electrolyte  $\text{O}_2$ , using the standard step-reformation process with first and second reformation voltages of 70 and 65 volts respectively,
- (6) two different sintered anode batches,
- (7) a combination of the standard and chemical impregnation processes.

### Conclusions

- (1) The processing details and preliminary electrical evaluation for capacitors made during this investigation are summarized in Table 4A, while the life test data are given in Table 4B. In all tests made, the best electrical results were obtained with the control batches, for which the standard pyrolytic conversion process was used.



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For example, the capacitance of chemically-impregnated units is considerably lower, the dissipation factor higher, and the DC electrical leakage and failure rates are inferior, indicating poor penetration and incomplete conversion of  $MnO_2$  in anode pores.

- (2) The effort of the impregnation-conversion technique overrides that of the reformation electrolyte used. Thus chemically impregnated capacitors display a higher failure rate than do capacitors impregnated by the standard method, even when the special  $O_2$  reformation electrolyte is used for the former units.
- (3) The results obtained with chemical impregnation are strongly dependent on all processing parameters including solution concentrations, dip cycle and time, and also on the physical characteristics (e.g., pore size and distribution) of the anodes. It is possible that a drying temperature higher than  $200^\circ C$  would provide better results - however the anticipated lower treatment temperature was the main reason for interest in chemical impregnation methods.

Since it is believed that more promising methods are known for circumventing or eliminating the effects of thermal damage during  $MnO_2$  impregnation of anodes than are offered by such chemical impregnation processes, further work is considered unwarranted.

#### (2) Further Studies of Reformation Electrolyte $O_2$

In the Fifth Quarterly Report, the results of some experiments with an improved reformation electrolyte  $O_2$  were described. Since the dissipation factor of units made using this electrolyte with standard reformation voltages (70/65 volts for 35 volt rated solid units) were higher than for capacitors reformed in the standard 0.01%  $H_3PO_4$  electrolyte, further investigations of the optimum reformation voltage for  $O_2$  were undertaken, as well as use of  $O_2$  in combination with several variations in the impregnation technique.

Since the results were mainly negative, they will not be reported in detail. At all reformation voltages listed (which ranged from 40 to 80 volts in 5 volt increments) for 35 volt rated completed solid units, the dissipation factor was somewhat higher than when a standard aqueous reformation electrolyte was employed. Moreover, the best reformation voltage, from the standpoint of DC leakage current and  $85^\circ C$ , 1000 hour life test reliability, was approximately the same (70/65 volts for 35 volt units) as for conventional reformation electrolytes. Modification of the  $MnO_2$  impregnation technique did not eliminate the dissipation factor increase, which appears to be characteristic of reformation in electrolyte  $O_2$ .

Further studies of this electrolyte are warranted, since the improvement in electrical performance on life test was again reproduced, and since the cause of the dissipation factor problem is believed to be known.

(c) Production and Life Testing of Large Pilot Batches of Solid Niobium and Niobium-Tantalum Alloy Capacitors

This work was discontinued during the last quarter to make the man power and processing and testing facilities available for the production of finished capacitor units for submission to the Bureau of Ships. This effort is described under Activity 10.

Activity 9 - Determination of Optimum Fill Electrolyte for Porous Anode Wet-Electrolyte Capacitors

A. Objective

The object of this phase is to determine the best operating electrolyte for wet capacitors with regard to compatibility with the dielectric, range of temperature operation, and dissipation factor.

B. Results of Recent Work

(a) Fill Electrolytes

After further studies of the S-class fill electrolytes, an electrolyte S<sub>4</sub> was finally chosen as offering the best combination of physical, chemical and electrical properties. The weight composition of electrolyte S<sub>4</sub> is 12% H<sub>2</sub>SO<sub>4</sub>, 35% ethylene glycol and 53% demineralized water. Boiling Point: 106°C; Freezing Point: about -35°C; Electrical Conductivity: 0.19 ohm cm<sup>-1</sup> at 25°C.

The variation of electrical characteristics with temperature cycling, for a small sample batch of 1.5 μf/100 volt pure niobium capacitors canned with this fill electrolyte, is given below. The electrolyte is compatible with all capacitor components at 85°C; with the dielectric layer formed on niobium-tantalum alloy anodes, at 85°C and 100 volts; and with the Nb<sub>2</sub>O<sub>5</sub> dielectric layer formed on pure niobium anodes, at +65°C and 100 volts.

Cap. No.	D.C. Leakage at 100V - I μa					Capacitance - C μf					Dissipation Factor %				
	25°C	-55°C	25°C	65°C	25°C	25°C	-55°C	25°C	65°C	25°C	25°C	-55°C	25°C	65°C	25°C
80	4.4	0.040	4.8	46.0	3.3	1.474	1.405	1.477	1.491	1.469	1.73	21.3	1.77	1.63	1.71
81	0.54	0.024	0.28	0.68	0.06	1.582	1.377	1.582	1.600	1.576	3.07	39.9	3.17	1.81	3.07
82	0.61	0.014	0.18	0.64	0.58	1.571	1.331	1.571	1.595	1.567	3.34	43.2	3.28	1.98	3.23
83	0.28	0.005	0.16	0.70	0.17	1.602	1.387	1.602	1.612	1.596	3.26	39.2	3.17	1.93	2.98
84	0.90	0.012	0.78	2.8	0.38	1.578	1.476	1.579	1.597	1.574	2.15	19.3	2.13	1.58	2.05

(b) Other Process Investigations

- (1) A considerable decrease in electrical leakage currents occurs after aging of capacitors at 120 volts and 25°C for 100 hours. This was found to be accompanied by a small decrease in capacitance and dissipation factor. The effect is due mainly to evolution of gas at defects in the dielectric layer, which are eventually plugged up by the gas bubbles. However, this gas generation results in excessive internal pressure buildup during subsequent life testing and eventually causes capacitor failures.
- (2) Reanodization of niobium anodes in hot fill electrolyte before canning did not improve the subsequent life test performance.
- (3) Life testing of pure niobium capacitors preheated to +85°C before final sealing did not reveal any beneficial results from this treatment.
- (4) Longer formation times (17 hours instead of 4 hours) for niobium anodes decreased the initial value of DC electrical leakage but did not eliminate the aging effect.
- (5) Aging of niobium anodes at 120 volts and 25°C or 85°C, for up to 150 hours in an open tank of fill electrolyte before canning, did not improve the subsequent electrical performance.
- (6) Aging of anodes in the cans before final sealing increased the dissipation factor without affecting the electrical leakage.
- (7) Anodes removed from capacitors which had failed on life test, when recanned using new components, displayed the same aging effect as before, although the initial leakages after recanning were considerably lower. After about 100 hours of life testing both original and recanned capacitors showed approximately the same leakage current levels and susceptibility to failure. This effect is illustrated in the following table, for a small sample of 22  $\mu\text{f}/100$  volt capacitors.

Leakage Current ( $\mu\text{a}$ )

Capacitor Number	Before Aging		After Aging		After 115 Hrs. Life Test at 85°C	
	Original Canning	Recanned	Original Canning	Recanned	Original Canning	Recanned
1	7.5	1.62	2.4	0.50	0.47	0.45
2	8.9	1.25	2.4	0.28	0.31	0.39
3	7.5	0.58	2.4	0.18	0.25	0.25

(c) Pilot Batches of Capacitors

Pilot production of larger (60-75 units) batches of pure niobium and niobium-tantalum alloy capacitors was continued during the last quarter. Life test results have verified a previous conclusion that the present technology will not produce pure niobium wet-electrolyte 100 volt units capable of continuous long-term service at +85°C. All such capacitors produced to date, even those employing fill electrolyte S<sub>4</sub>, have failed before 800 hours of life test have elapsed. This particular combination of voltage and temperature appears to result in either electrochemical attack or in crystallization of the amorphous oxide layer, with even the best fill electrolytes found to date. Thus the electrical leakage gradually increases with time on life test until the capacitors eventually burst due to internal gas pressure buildup.

On the other hand, it has been found possible to make successfully the following capacitor types:

- (1) 1.5  $\mu$ f/100 volt and 20  $\mu$ f/100 volt units from pure niobium anodes, capable of operation at +65°C.
- (2) 2.5  $\mu$ f/100 volt and 22  $\mu$ f/100 volt units from niobium - 81% tantalum alloy anodes, capable of operation at +85°C. Units of these types have survived 1000 hours (in some cases up to 3500 hours) of life testing with little or no degradation in electrical performance.

It is believed that equally good capacitors could be made from niobium-tantalum alloy materials containing 50% tantalum or lower. Unfortunately, the supply of lower tantalum content alloy powders (25% tantalum and 50% tantalum) was exhausted during pilot production of solid electrolytic capacitors and in studies of optimum powder particle size distribution for wet-electrolyte capacitors.

Activity 10 - Production and Testing of Pure Niobium and Niobium Alloy Porous Anode Capacitors of Wet and Solid-Electrolyte Types

Sub-Activities 10.1 and 10.3 - Solid Niobium and Niobium Alloy Capacitors

Eight batches of niobium and niobium-tantalum alloy capacitors consisting of twenty-four units per batch, were made and tested for delivery to the Bureau of Ships in Washington, D. C. in partial fulfillment of the terms of the contract.

All batches were subjected to 1000 hours life testing at 85°C and rated voltage. The average electrical characteristics of each capacitor type after life testing are summarized in Table 5. In addition, samples of these capacitors, subjected to the following Quality Control Tests under specified conditions, were found to meet the pertinent Military Specifications MIL-C-26655 for solid tantalum capacitors:

- (1) Shock testing
- (2) Vibration testing
- (3) Temperature stability testing (-55°C to +125°C)
- (4) Surge voltage testing (85°C, 120% rated voltage, 125°C, 80% rated voltage)
- (5) Temperature cycling (-55°C to +125°C)
- (6) Humidity testing

Although the pure niobium and niobium alloy units withstood the short term tests at 125°C, they cannot be recommended for extended use at this temperature, even with an appropriate voltage derating. The maximum allowable operational temperature for long-term performance stability is +85°C.

#### Sub-Activities 10.2 and 10.4 - Wet Niobium and Niobium Alloy Capacitors

Four batches of niobium and niobium-tantalum alloy capacitors, consisting of twenty-four units per batch, were made and tested for delivery to the Bureau of Ships in Washington, D. C. in partial fulfillment of the terms of the contract.

All batches were subjected to at least 250 hours of life testing at 100 volts and rated temperature (either +65°C or +85°C). The average electrical characteristics of each capacitor type, after testing, are summarized in Table 5. Other lots of the same capacitor types are continuing on life test under specified conditions - in the case of 100 volt, 65°C units, the electrical characteristics of the best lots are still stable after more than 3000 hours on test.

In addition, samples of these capacitors, subjected to the following Quality Control Tests under specified conditions, were found to meet the pertinent Military Specifications of MIL-C3965 for wet tantalum capacitors.

- (1) Shock testing
- (2) Vibration testing
- (3) Temperature stability testing (-55°C to +65°C).
- (4) Terminal strength testing
- (5) Surge voltage testing
- (6) Barometric pressure testing.

The maximum recommended operating temperature for the 100 volt pure niobium wet-electrolyte units is +65°C, while for the 100 volt niobium-tantalum alloy units it is +85°C.

Task B, Activity 5 - Determination of Optimum Fill Electrolyte for Niobium and Niobium Alloy Foil Capacitors

A. Objective

The purpose of this work is to determine the best fill electrolyte from the standpoint of conductivity, range of temperature operation, and compatibility with the metal-amorphous oxide system and other capacitor components.

B. Results of Recent Work

(1) 100-Volt Units for Operation at 85°C

(a) Pure Niobium Foil

Further work has substantiated a previous observation that all 100 volt, 85°C capacitors made from pure niobium foil eventually build up a high internal gas pressure when put on life test. An increase in DC leakage is accompanied by an appreciable loss in capacitance and increase in dissipation factor (Figures 1 and 2, 3A and 3B). The effect appears to be due to a combination of both voltage and temperature (i.e., electro-chemical attack), since capacitors placed on test at 85°C with no applied voltage remain unchanged in electrical characteristics, and since 100 volt, 65°C capacitors display a less rapid deterioration with time on life test.

Since the rate of change of capacitance and dissipation factor with time (Figures 1 to 3B) is most marked during the first twenty-four hours of life test, it was at first believed that electrolyte loss was occurring. However, the weight loss was found to be quite small (approximately 0.4% of the electrolyte for all 100 volt, 85°C groups after twenty-four hours testing, and about 3% of the electrolyte after 1500 hours testing), compared with the corresponding capacitance loss. Moreover, although these capacitors displayed high dissipation factors (2 to 3 times the initial values) after about 400 hours of testing, the dissipation then gradually decreased again to the initial value upon further testing. This indicates that there was still sufficient fill electrolyte in the paper winding to provide a low resistance connection between anode and cathode foils.

Most 100 volt, 85°C pure niobium units did not survive 1000 hours of life testing. Samples of both failed capacitors and operating survivors, when cut open and examined, in all cases showed evidence of crystallization of the amorphous oxide layer after 800 to 1000 hours testing.

Due to this steady deterioration during life test, it is not considered feasible to produce 100 volt, 85°C wet electrolyte foil capacitors from pure niobium, at least with the present technology.

(b) Niobium-Tantalum Alloy Foil

Further work has been carried out on 100 volt, 85°C units processed from niobium-tantalum alloys containing 75%, 50% and 25% niobium by weight, in an effort to identify the best alloy for preparation of capacitors to be submitted to the Bureau of Ships. In the following table, the electrical characteristics of these capacitors are compared after 3000 hours of life testing. In addition, Figures 1 and 2 illustrate graphically the percentage change of capacitance and dissipation factor with test time for these alloy and pure niobium units.

Measurements at 25°C, Rated Voltage

	D.C. Leakage $\mu$ a		Capacitance $\mu$ f at 120 cycles		Dissipation Factor % at 120 cps	
	0 hours	3000 hours	0 hours	3000 hours	0 hours	3000 hours
75% Ta-25% Nb	4.1	0.18	5.58	5.64	1.9	1.8
50% Ta-50% Nb	3.8	0.22	5.70	5.62	1.7	2.0
25% Ta-75% Nb	6.3	2.7	5.98	4.61	1.7	3.3
100% Nb-Control	1.1	2.5	6.38	3.65	1.6	3.8

It is clear from the results that the capacitor quality decreases with increasing niobium content. Although the 75% tantalum-25% niobium and the 50% tantalum-50% niobium alloy units are still satisfactory after 3000 hours testing, it appears that there is a definite relationship between niobium content, electrical characteristics and time.

(2) 100 Volt Units for Operation at 65°C

Based on the experience with porous anode wet electrolyte units, it was thought that production of an acceptable 100 volt, 65°C unit from pure niobium foil might be possible. Accordingly, two groups of this capacitor type were made and put on life test. The variation of electrical characteristics with test time are outlined in the table below.

Measurements at 25°C, 100 Volts

Batch No.	D. C. Leakage - $\mu$ a			Capacitance, $\mu$ f at 120cps			Dissipation Factor % at 120 cps		
	0 hrs.	600 hrs.	1500 hrs.	0 hrs.	600 hrs.	1500 hrs.	0 hrs.	600 hrs.	1500 hrs.
1	12.3	1.59	3.3	6.11	5.69	5.47	2.0	5.4	7.0
2	5.2	0.42	1.8	5.50	5.53	5.44	1.7	2.7	4.2

From the results, it appears that the lower test temperature merely slows down the gradual degradation of electrical characteristics.

(3) 50 Volt Units for Operation at 85°C

Three groups of 50 volt, 85°C capacitors were processed from pure niobium foil, using different formation voltages and formation techniques.

The first batch was anodized at 200 volts in a small formation tank and then split into two groups, one for operation at 50 volts, 85°C and the other for 100 volts, 85°C operation. The results after 1500 hours of life testing, summarized in the table below, are very interesting.

Measurements at 25°C, Rated Voltage

	D.C. Leakage $\mu$ a			Capacitance, $\mu$ f at 120 cps			Diss. Factor % at 120 cps			Yield %		
	0 Hrs.	800 Hrs.	1500 Hrs.	0 Hrs.	800 Hrs.	1500 Hrs.	0 Hrs.	800 Hrs.	1500 Hrs.	0 Hrs.	800 Hrs.	1500 Hrs.
85°C, 50 Volt Operation	9.0	0.14	0.17	7.90	8.01	8.26	1.9	1.5	1.6	100	100	100
85°C, 100 Volt Operation	23.0	4.5	All Failed	7.80	3.58	All Failed	1.8	2.2	All Failed	80	40	0

It is evident that there is a marked difference in the activity of the fill electrolyte when the operating voltage is decreased from 100 to 50 volts at 85°C.

Two other groups of 50 volt, 85°C pure niobium foil capacitors were processed using a large formation tank to improve the formation conditions. The only difference in these two foil groups was that one was formed to 150 volts and the other to 160 volts. The electrical characteristics of these capacitors are compared with those of similar capacitors formed to 200 volts.

Measurements at 25°C, 50 Volts

Formation Voltage Volts	D.C. Leakage $\mu$ a			Capacitance $\mu$ f at 120 cps			Diss. Factor % at 120 cps		
	0 Hrs.	800 Hrs.	1500 Hrs.	0 Hrs.	800 Hrs.	1500 Hrs.	0 Hrs.	800 Hrs.	1500 Hrs.
150	1.4	0.13	0.09	9.6	10.3	10.3	2.0	1.7	1.6
160	0.70	0.10	-	9.9	9.5	-	2.0	1.4	-
200	9.0	0.13	0.17	7.9	8.1	8.2	1.9	1.5	1.6



The results indicate good stability in electrical properties for 50 volt units, and little or no effect from the use of a lower formation voltage. Moreover, no evidence has been found of the buildup of internal gas pressure or crystallization of the dielectric layer, in some of these units which have been cut open for examination.

(4) 75 Volt Units for Operation at 85°C

Because of the success achieved with the 50 volt, 85°C units, an attempt was made to produce a 75 volt, 85°C capacitor using pure niobium foil. Life test results on one group of these capacitors indicated the same characteristic loss of capacitance and increase in dissipation factor as was encountered with the 100 volt, 85°C units (see Figure 3A and 3B). Moreover, examination of one of these units after 800 hours of life testing disclosed signs of serious pressure buildup and crystallization of the dielectric layer. In fact, there appears to be little difference in behavior between 100 volt, 85°C capacitors and 75 volt, 85°C capacitors, so far as rate of electrical degradation is concerned.

Task B, Activity 7 - Production and Testing of Pure Niobium and Niobium Alloy Foil Capacitors of Wet Electrolyte Type

Sub-Activities 7.1 and 7.2

One batch of pure niobium foil capacitors and one batch of niobium-tantalum alloy foil capacitors, consisting of twenty-four units per batch, were made and tested for delivery to the Bureau of Ships in Washington D. C. in partial fulfillment of the terms of the contract.

The capacitors have been subjected to at least 600 hours of life testing at 85°C and rated voltage (50 and 100 volts). The average electrical characteristics after testing are listed below.

Batch No.	Description	Capacitor Type C $\mu$ f/V volts	Can Size	Average Electrical Characteristics at Rated Voltage, 25°C		
				D.C. Leakage $\mu$ a	Capacitance $\mu$ f at 120 cps	Diss. Factor % at 120 cps
1	Pure niobium foil wet electrolyte.	10/50	C3	0.13	9.96	1.73
2	Nb-50% Ta alloy foil wet electrolyte.	5.6/100	C3	0.088	5.63	2.48

Samples of these capacitors, on life test for more than 2500 hours under specified conditions, have shown no degradation in electrical performance. Other samples of these capacitors, subjected to the following Quality Control tests under specified conditions, were found to meet the pertinent Military Specifications MIL-C-3965 for tantalum foil capacitors:

- (1) Temperature stability testing
- (2) Vibration testing
- (3) Temperature and immersion cycling
- (4) Surge voltage testing
- (5) Moisture resistance testing
- (6) Reduced pressure testing

The maximum recommended operating temperature for both capacitor batches, at rated voltage or lower, is +85°C.

## SECTION 2 - TECHNICAL SUMMARY OF THE PROGRAM

### Task A - Work on Niobium and Niobium Alloy Porous Anode Capacitors of Wet and Solid Types

#### Activity 1 - Trace Impurity Analyses of Niobium Materials Made by Different Processes

Exhaustive trace impurity analyses were carried out on pure niobium materials made by three different processes - hydrogen reduction of pentachlorides, carbothermic reduction of oxides, and a proprietary process. Of the three materials as received, the hydrogen-reduced niobium appeared to be the purest.

This analytical work, in conjunction with subsequent electrical evaluation of the materials in the form of capacitor anodes, enabled a tentative purity specification for capacitor-grade niobium powder to be written.

In this activity, development of improved analytical techniques was required to obtain adequate detection sensitivity for certain impurities, such as Zr, Ti, V, Sn, Al, Si, and Li.

The work is described in complete detail in Technical Report No. P-63-11, a copy of which will be furnished to the Bureau of Ships as part of the Engineering Specifications.

#### Activity 2 - Preparation of Niobium-Tantalum Alloy Powders

A vacuum sintering method of alloying tantalum and niobium powders was developed and used to make alloys containing 26.3, 51.1, 57.3, 80.8 and 100% by weight tantalum. The homogeneity was checked by metallographic and electron microprobe techniques and found to be comparable with that of electron-beam melted samples. The purity of the materials was very high, although the nitrogen contents were somewhat greater than desired.

The work is described in detail in Technical Report P-63-9, a copy of which will be furnished to the Bureau of Ships as part of the Engineering Specifications.

### Activity 3 - Optimum Conditions for Removal of Carbon from Niobium

A vacuum prepurification heat treatment of niobium materials at 2100°C and 2300°C and the effect of doping materials with oxygen by anodization, were investigated, in an effort to reduce the levels of metallic (e.g. iron) and non-metallic impurities (e.g. carbon) in capacitor-grade materials. It was found from analytical and electrical evaluations that such prefurnacing treatment does not yield any advantage, provided a temperature of 2100°C for at least thirty minutes is used in sintering capacitor anodes. An atomic ratio of 10 - 20 to 1 of oxygen to carbon is needed for removal of carbon to the 20 ppm level during sintering; on the other hand, excessive oxygen levels in sintered anodes can also impair their performance. Most metallic impurities are readily removed to low levels by volatilization during sintering.

### Activity 4 - Optimum Anodization Conditions for Niobium Anodes

Extensive studies were carried out to determine the best anodization conditions, formation electrolyte, time, temperature, current density, electrolyte agitation and ratio of formation voltage to solid operating voltage.

A total of thirteen electrolytes were tested on the basis of terminal leakage currents, and breakdown voltages. The electrolyte conductivity, which was studied over a wide range for the better electrolytes, was found to exert a marked influence on the breakdown voltages of anodes (Figure 2, Third Quarterly Report). A reliable well-defined correlation between wet test evaluations and subsequent solid test electrical performance of anodes was not uncovered. It was found that a formation temperature of 25°C or lower must be used, in order to form oxide films with the best possible dielectric properties, and that formation times in excess of four hours do not improve solid test performance of completed capacitors. Current density and electrolyte stirring are important mainly because of the effect on the electrolyte temperature in the vicinity of the anodes.

### Activity 5 - Optimum Processing Conditions for Niobium Anode Solid Electrolyte Capacitors

Detailed studies were made to optimize the following processing steps:

- (1) Conversion of raw materials into capacitor-grade powder.
- (2) Methods for sizing, blending and pressing of powders into anodes.
- (3) Sintering conditions for anodes.
- (4) Storage methods for sintered anodes.
- (5) Pre-formation and post-formation chemical cleaning of anodes.
- (6) Preheating and reanodization of formed anodes prior to pyrolysis.

- (7) Semiconductor impregnation of formed anodes.
- (8) Reformation of anodes.
- (9) Carbon and silver coating and canning of impregnated anodes.
- (10) Aging of canned capacitors.

Since these studies were discussed in some detail in the Quarterly Reports, only the more salient points will be mentioned here:

#### Powders

It was found to be essential to minimize pickup of oxygen and nitrogen during pulverizing by conducting the milling operation in an argon atmosphere. It is important to remove ultra fine particles (particle sizes less than one micron) from size-reduced materials before blending them into capacitor-grade powders. A simple method of effecting this removal, by a water sedimentation technique, was successful. The most suitable niobium particle size distribution for pressing porous anodes (geometric mean size about 29 microns) is relatively coarse compared with powder blends used for similar-sized tantalum anodes (geometric mean sizes down to 15 microns). Use of a parameter (geometric mean size), which typifies any powder blend by a single number measuring the average particle size, was found to be convenient.

#### Anodes

A minimum green density of about 5.0 gms/cc was found to be necessary to obtain niobium anodes of suitable mechanical strength and pore structure after sintering; pore diameters less than 1 or 2 microns are undesirable since they tend to close up during anodization and are then virtually impossible to impregnate with  $MnO_2$ . A sintering temperature of 2100°C for thirty minutes was found to be necessary to obtain anodes of satisfactory chemical purity. Placing of anodes in demineralized water in polyethylene containers immediately after sintering was found to be the most satisfactory method of storage prior to anodization. Even in this case, it is important to utilize anodes as quickly as possible after sintering. If anodes are stored for prolonged periods of time before use, a pre-cleaning in AR-grade acetone followed by thorough rinsing, before anodization, provides better finished capacitors. Preformation cleaning treatments in nitric acid were found to offer no improvement in solid capacitor properties. Pre-etching treatments in bromine-methanol or hydrofluoric acid solutions were found to degrade the electrical performance of anodes, probably because of the difficulty of removing reaction products from the complex internal pore network. Similarly post-formation etching treatments, followed by reanodization, although apparently improving wet test properties, did not result in improvement of solid capacitor performance.

#### Impregnation of Anodes and Reformation

It was found to be important to keep the conversion temperature below 280°C during pyrolysis of  $Mn(NO_3)_2$  to form  $MnO_2$  in niobium anode pores, in order to minimize thermal damage.

Chemical impregnation techniques, for depositing  $MnO_2$  in anode pores and requiring a maximum reaction temperature of  $200^\circ C$ , yielded capacitors with much poorer electrical properties than units impregnated in the standard manner. Other impregnation modifications tested did not substantially improve capacitor performance.

A non-aqueous reformation electrolyte was developed which markedly reduced the leakage currents and  $85^\circ C$  life test failure rates of canned capacitors.

#### Aging

It is important to avoid a combination of voltage stress and thermal stress during initial stages of aging. The canned units are therefore first aged at room temperature at a series of voltages ranging from rated voltage up to about 140% of rated voltage.

#### Activity 6 - Preparation of Highly Purified Niobium Powders

About 2.5 pounds of ultra high purity niobium metal, in the form of roundels, were prepared using a specially developed ion-exchange purification method. The method is described in detail in Technical Report No. P-63-13, a copy of which will be furnished to the Bureau of Ships as part of the Engineering Specifications. Although of much higher purity than other capacitor-grade niobium materials investigated, this material did not yield anodes with superior electrical properties.

High purity niobium microspheres were prepared by plasma arc melting of niobium wire. Although this material, when made into a standard size distribution powder, provided anodes with acceptably low leakage currents on solid test, the dissipation factors were high and the size factors inordinately low.

#### Activity 7 - Optimum Anodization Conditions for Niobium Alloy Solid Electrolyte Capacitors

The optimum anodization conditions for niobium-tantalum alloy anodes were found to be the same as for pure niobium anodes. Most electrical properties (breakdown voltage, terminal leakage current, size factor) on wet test improve with increasing tantalum content of the alloys; and this conclusion appears to apply also to electrical performance of completed solid units on life test at  $85^\circ C$ .

#### Activity 8 - Optimum Processing Conditions for Niobium-Alloy Solid Electrolyte Capacitors

Insufficient alloy material was available to carry out a separate detailed study of all processing parameters. Processing conditions developed for pure niobium anodes were found to be equally satisfactory for the alloy materials under study.

Activity 9 - Optimum Fill Electrolyte for Porous Anode Wet Capacitors

Although a large number of fill electrolytes were tested, an electrolyte compatible with the Nb-Nb<sub>2</sub>O<sub>5</sub> system at 85°C and 100 volts and possessing satisfactory electrical conductivity over the temperature range from -55°C to +85°C was not found. However, an electrolyte suitable for use in 100 volt niobium-tantalum alloy capacitors up to 85°C, and in 100 volt pure niobium capacitors up to 65°C, was eventually developed after considerable effort.

Activity 10 - Production of Pure Niobium and Niobium Alloy Porous Anode Wet and Solid Electrolyte Capacitors for Delivery to the Bureau of Ships

After a period of pilot production and testing of various capacitor types, eight batches of solid niobium and niobium-tantalum alloy capacitors in A, B, C and D case sizes, and with 35 and 50 volt ratings, were made and subjected to life testing and environmental testing. Having been found to meet Military Specifications for similar tantalum capacitor units, these batches were submitted to the Bureau of Ships in Washington, D. C. for evaluations, in quantities of twenty-four units per batch.

After a similar pilot development effort, four batches of 100 volt wet niobium and niobium-tantalum alloy capacitors in T1 and T3 case sizes were made, tested, and submitted to the Bureau of Ships for evaluation.

The processing details for these capacitors are given in Kemet Technical Report K-1963, a copy of which will be furnished to the Bureau of Ships as part of the engineering specifications.

Task B - Work on Niobium and Niobium-Alloy Foil Capacitors

Activity 1 - Preparation and Testing of Pure Niobium 0.010" Thick Sheet Made from Two Different Materials

Plates of pure niobium, made by electron beam purification and by a proprietary process, were rolled into 0.010" thick sheet. Portions were then subjected to different metallurgical treatments as follows:

- (1) strained sheet as rolled.
- (2) stress-relieved foil.
- (3) recrystallized foil or smallest grain size.
- (4) recrystallized foil pack rolled between niobium cover plates.

Samples were analyzed for interstitial impurities, and test specimen samples were evaluated on wet test for breakdown voltage and terminal leakage current. In each case, the quality was found to be comparable with that of commercially available niobium capacitor-grade foil.

Activity 2 - Preparation and Testing of Five Different Niobium-Tantalum Alloys  
in the Form of 0.010" Thick Sheet

Alloy ingots containing 0, 25, 50, 75, and 100% by weight tantalum were prepared by electron beam melting of suitable proportions of pure niobium and tantalum materials. Pieces of the ingots were then rolled into 0.010" thick sheet and recrystallized. Electrical evaluation of test specimens of foil showed a progressive improvement in quality with increasing tantalum content. This observation was corroborated by subsequent life testing of completed capacitor units made from 0.0005" thick foil, which indicated that even an alloy containing 50 percent tantalum by weight is inferior to pure tantalum material.

Activity 3 - Preparation and testing of Niobium-Platinum and Niobium-Zirconium  
Alloys in the Form of 0.010" Thick Sheet

Alloys containing 0.1% by weight platinum and 1.0% by weight zirconium were prepared by electron beam melting of pure constituent materials. Pieces of alloy were then rolled into 0.010" thick sheet and recrystallized, while other portions were rolled into unannealed 0.0005" thick foil. Since electrical evaluation of test specimens indicated that the niobium-platinum and niobium-zirconium alloys were inferior to the niobium-tantalum alloys described above, no further work was done on these alloy materials.

The preparation of the pure niobium and niobium alloy foil materials discussed under Activities 1, 2, and 3 is fully described in Technical Report No. HS-1, a copy of which will be furnished to the Bureau of Ships as part of the Engineering Specifications.

Activity 4 - Optimum Processing Conditions for Niobium and Niobium Alloy Foils

A superior formation electrolyte for niobium and niobium alloy foil materials was developed, after testing of a large number of electrolytes. As in the case of oxide formation on porous anodes, the electrolyte conductivity was found to have a critical influence upon the breakdown and electrical quality of the anodic oxide layer formed on foil. The optimum electrolyte resistivity is much higher (approximately  $3 \times 10^4$  ohm cm) than for niobium porous anodes. The optimum formation temperature is 0°C or lower, although 25°C formation will also produce satisfactory dielectric films.

Vacuum pre-furnacing of foil before anodization, although resulting in much better surface purification than can be accomplished by chemical etching techniques, is impractical for the rather long strips of foil used in finished capacitors. An etching solution was found which provides satisfactory surface cleaning prior to anodic oxide formation.

Activity 5 - Optimum Fill Electrolyte for Niobium and Niobium-Alloy Foils

After extensive examination of various fill electrolytes, one was found which makes possible the manufacture of 100 volt foil capacitors capable of operation up to 85°C, provided that a niobium-tantalum alloy material is used.

Although this same electrolyte is not suitable for use in a similar pure niobium foil capacitor, due to eventual crystallization of the  $Nb_2O_5$  dielectric layer after approximately 1000 hours of life testing, it can be used to make pure niobium units of 50 volts rating.

#### Activity 6 - Rolling of Selected Niobium and Niobium-Alloy Materials into Capacitor Grade Foil

Portions of all pure niobium and niobium alloy materials, described under Activities 1, 2 and 3, were converted into 0.0005" thick capacitor-grade foil. The foils were not annealed after final rolling, since it was found that such treatment had little or no effect on electrical characteristics, and increased the possibility of surface contamination of the foil.

#### Activity 7 - Production and Testing of Niobium and Niobium Alloy Foil Capacitors for Submission to the Bureau of Ships

After a period of experimental pilot production and testing of large capacitor batches, two batches consisting of 24 units each were made and tested for submission to the Bureau of Ships. One batch, made from a 50% niobium - 50% tantalum alloy foil, is rated at 100 volts at a maximum operating temperature of 85°C, while the other batch, made from pure niobium foil, is rated at 50 volts at +85°C.

The processing details for these capacitors are also given in Kemet Technical Report K-1963.

#### Task C - Fundamental Studies of Niobium and Tantalum Single Crystals and Foil

In the basic studies of anodic oxide films formed on niobium and tantalum, the main investigation was focused on high purity foil and single crystal specimens.

In the first phase, except for some exploratory and confirmatory experiments, anodizing conditions (electrolyte composition, current density and temperature) were kept constant. The progress of anodization was followed to breakdown of the dielectric films by electron microscopy using carbon replicas or, in some cases, the isolated oxide films themselves. Minor defects in the amorphous films on niobium foil and single crystals were noted at quite low voltages, and their development into catastrophic ruptures with increasing voltage was followed. In contrast, similar defects appeared with tantalum specimens only at much higher voltages. Unique with the niobium specimens was the occurrence of white powder spots in the anodic films upon breakdown - subsequent examination by X-ray diffraction methods identified this material as a crystalline form of  $Nb_2O_5$ . Thermal oxidation experiments on niobium and tantalum anodized foils confirmed the greater susceptibility of amorphous  $Nb_2O_5$  films to growth of crystallite areas, especially in the presence of surface contaminants such as fluorides. Further work should be carried out to determine the origin and growth mechanism of the various types of film defects observed in these studies.



In a second phase, the influence of electrolyte composition and electrolyte temperature in suppressing the formation of defects in oxide films on foil, was studied in some detail. This work has confirmed the important role of electrolyte selection in improving film quality, an observation hitherto based mainly on electrical measurements. Thus the superior electrical properties of films formed with the best electrolyte was shown to be due to a much lower density of defects in the anodic film formed at a given voltage, and especially to the absence of crystalline areas. The reasons for the superiority of one electrolyte over another are not fully understood at present. Similarly, an interesting difference in optimum formation conditions for niobium and tantalum, previously concluded from electrical evaluation data, was confirmed: for tantalum pentoxide films, the defect density tends to decrease with increasing formation temperature, over the range 0°C to 90°C, whereas for niobium pentoxide films, the converse is true.

In another study, it was found, somewhat surprisingly, that surface flaws in single crystals (e.g. mechanical deformation, subgrain boundaries and precipitated carbide particles) apparently do not provide preferred nucleation sites for breakdown of the anodic films. Similarly the crystallographic orientation of the crystals appears to bear no relationship to the type or density of defects. Finally, surface conditions of the crystals, as controlled by mechanical, electrolytic or chemical polishing, also seems to have very little effect upon film quality. In contrast to this result, in the case of polycrystalline foil specimens, vacuum furnace specimens provided relatively high quality anodic films at high voltages in comparison with mechanically polished or chemically-cleaned foil specimens.

### SECTION 3 - GENERAL CONCLUSIONS

The work carried out during this program has confirmed that, compared with tantalum, niobium is inherently a more difficult material to contend with for capacitor applications. Thus the optimum processing conditions, from the initial conversion of bulk niobium into capacitor-grade powder to the final hermetic sealing of anodes in metal cans, are in many cases different from those employed for tantalum capacitor production, and also rather more critical. For example, it has been found, from both X-ray diffraction and electron microscopic studies, that the production of crack type defects and crystallized areas in an amorphous niobium pentoxide layer, due to application of temperature stress or voltage stress or a combination of the two, and the consequent degradation of electrical properties, are much more readily induced than in the case of tantalum pentoxide films. This is true not only during such "wet" processing stages as formation, reformation and pyrolytic impregnation, but also during subsequent aging and life testing at rated voltage and temperatures as low as 85°C. Moreover, even with the applications of careful temperature controls and special processes, the electrical performance of completed niobium capacitors, although meeting the pertinent Military Specifications is, in general, not as good as for comparably rated tantalum units, insofar as electrical leakage and high temperature (85°C) operational reliability are concerned. This is particularly true for the porous anode and foil wet-electrolyte capacitors, for which problems are encountered with instability of the Nb-Nb<sub>2</sub>O<sub>5</sub> system in the presence of a liquid electrolyte at 85°C and 100 volts.

TABLE 1

Task A, Activity 5

PHYSICAL PARAMETERS FOR AGGLOMERATED ANODES

Lot Designation	Agglomeration Temp. °C	Before Agglomeration		After Agglomeration		Before Sintering		After Sintering at 2100°C		Net * Breakdown Voltages V <sub>BD</sub> Volts
		Powder Size	Pressed Slab Density gms/cc	Slab Density gms/cc	% Increase in Density	Powder Distribution	Anode Density gms/cc	Anode Density gms/cc	% Increase in Density	
A	2200	-400 Mesh	4.81	5.78	20.2	36.8% 170/230 63.2% 230/325	5.33	5.52	3.55	393
B	1800	-400 Mesh	4.94	5.75	16.4	36.8% 170/230 63.2% 230/325	5.13	5.44	6.10	348
C	1500	-400 Mesh	5.00	5.02	0.4	36.8% 170/230 63.2% 230/325	5.13	5.44	6.15	365
D	1200	-400 Mesh	4.97	4.98	0.2	36.8% 170/230 63.2% 230/325	5.06	5.40	6.68	373

\* Breakdown voltage tests were conducted in electrolyte Y<sub>1</sub> at 25°C and a formation current density of 25 ma/gm.

TABLE 2 Task A, Activity 5

WET ELECTRICAL PROPERTIES FOR ANODES PRESSED FROM AGGLOMERATED NIOBIUM POWDERS

Plug Designation	Avg. Plug		Bias, Volts	Capacitance and Dissipation Measurements*						d-c Terminal Leakage at 25°C	
	Weight gms	Density g/cc		Tested at 120 cps		Tested at 1000 cps		150 Volts $\mu\text{a}/\mu\text{f}$	200 Volts $\mu\text{a}/\mu\text{f}$		
				A	S'	% Diss.	A			S'	% Diss.
A-2200C	0.494	5.52	0	2.52	228	1.58	2.47	223	.838	26.4	
			5	2.47	224	1.06	2.45	222			
			12	2.46	223	0.90	2.43	220			
			35	2.44	221	0.94	2.42	219			
B-1800C	0.470	5.44	0	2.65	236	1.95	2.58	230	.724	23.8	
			5	2.60	231	1.26	2.56	228			
			12	2.57	229	1.10	2.55	227			
			35	2.56	228	1.02	2.54	226			
C-1500C	0.469	5.44	0	2.57	229	2.17	2.51	224	.783	25.3	
			5	2.52	225	1.26	2.49	222			
			12	2.50	223	1.06	2.48	221			
			35	2.49	222	0.99	2.46	219			
D-1200C	0.464	5.40	0	2.99	265	2.99	2.88	255	.771	26.2	
			5	2.91	257	1.78	2.86	253			
			12	2.87	254	1.43	2.86	253			
			35	2.86	253	1.19	2.83	250			

D.C. terminal leakage currents measured in  $Y_1$ , other wet tests in 30%  $\text{H}_2\text{SO}_4$ . Averages of five results.

\* Formation voltage  $V_f = 200$  volts at 25°C. The A and S' values have been normalized to the equivalent formation voltage at 90°C = 164.2 volts.

A = charge number in millicoulombs/g S' = size factor in millicoulombs/in<sup>3</sup>.

TABLE 3 Task A, Activity 5

POROSIMETER RESULTS FOR ANODES PRESSED FROM AGGLOMERATED NIOBIUM POWDERS

Designation	Agglomeration Temperature °C	Density gm/cc	Total Porosity Per Cent	Per Cent of Total Porosity in Given Apparent Pore Diameter Range (Microns)						Calculated Surface Area cm <sup>2</sup> /gm*		
				>15	15-10	10-7	7-5	5-3	3-1.5		<1.5	Average
A	2200	5.82	33.5	-	-	35	33	17	11	4	6.3	198
B	1800	5.44	35.6	-	-	35	38	16	7	4	6.5	207
C	1500	5.44	36.5	-	-	22	49	19	7	3	6.1	201
D	1200	5.40	40.4	-	-	1	61	28	8	2	5.3	231

\* Calculated from wet capacitance measurements using  $C = \frac{AK}{36\pi \cdot 10^5 \cdot t \cdot g}$

K = Dielectric Constant

A = Area in cm<sup>2</sup>

t = Dielectric Thickness in cm

C = Capacitance in μf

g = Anode Weight in grams

TABLE 4A Task A, Activity 5.5

PROCESS DETAILS FOR CHEMICAL IMPREGNATION OF NIOBIUM CAPACITORS, AND PRELIMINARY ELECTRICAL RESULTS

Concentration of solutions used for chemical impregnation:

12.4 gms of  $\text{NaMnO}_4$  . 3  $\text{H}_2\text{O}$  per 100 cc of solution (batches 43, 44, 45 and 46).

6.2 gms of  $\text{NaMnO}_4$  . 3  $\text{H}_2\text{O}$  per 100 cc of solution (batches 47, 48 and 52).

147 gms of  $\text{Mn}(\text{NO}_3)_2$  . 6  $\text{H}_2\text{O}$  pe. 100 cc of solution (all batches).

Batch No.	Material	12 V. Bias Wet Test in $\text{H}_2\text{SO}_4$ Soln.		Preparation				Leakage Current - $\mu\text{a}$ , 35 Volts		120 cps, 35 Volts		1 Kcps, 35 Volts		Yield After Canning		
		C- $\mu\text{f}$	D.F.-%	Method of Impreg.	Cycle No.	Time-Mins.		Reformation Electrolyte	High	Low	Avg.	C- $\mu\text{f}$	D.F.-%		C- $\mu\text{f}$	D.F.-%
						Dip	Dry									
43-A	402 Lot 1	8.7	1.1	Chem.	4/4	2	2	$\text{O}_2$	27.0	1.5	12.8	1.7	20.2		8/10	
				Chem.	4/4	2	2	0.01% $\text{H}_3\text{PO}_4$	34.0	6.0	19.7	3.2	33.5		10/12	
			Chem.	3/2	2	2	2	0.01% $\text{H}_3\text{PO}_4$	31.0	13.0	20.2	4.7	20.5		8/10	
			Std.	4/4	-	-	-	0.01% $\text{H}_3\text{PO}_4$	6.9	0.48	1.6	13.3	1.7		10/10	
44-A	402 Lot 1	8.7	0.6	Chem.	4/4	2-3	4	$\text{O}_2$	10.0	1.1	3.6	9.8	3.2	9.52	9/10	
				Chem.	4/4	2-3	4	0.01% $\text{H}_3\text{PO}_4$	12.0	1.8	6.3	10.1	4.7	9.54	10/10	
			Chem.	3/2	4	4	4	0.01% $\text{H}_3\text{PO}_4$	7.4	0.06	1.9	10.0	5.3	9.43	10/10	
			Std.	4/4	-	-	-	$\text{O}_2$	3.9	0.92	2.5	13.9	3.1	13.63	9/10	
45-A	402 Lot 2	8.4	2.4	Chem.	4/4	3-5	4	$\text{O}_2$	74.0	5.3	19.3	9.3	5.1	8.74	9/10	
				Chem.	4/4	3-5	4	0.01% $\text{H}_3\text{PO}_4$	170.0	6.3	39.9	7.0	30.4	4.1	56.0	10/10
			Chem.	3/2	4	4	4	0.01% $\text{H}_3\text{PO}_4$	22.0	1.1	7.2	8.7	14.3	7.1	29.9	10/10
			Std.	4/4	-	-	-	$\text{O}_2$	0.69	0.08	0.46	14.0	3.7	13.5	25.6	10/10
46-A	402 Lot 1			Chem.	4/4	3-5	4	$\text{O}_2$	7.4	1.2	4.3	9.3	3.6	8.9	7/8	
				Chem.	3/2	3-5	4	$\text{O}_2$	57.0	0.28	10.3	9.5	3.1	9.2	12.8	8/9
			Std.	4/4	-	-	-	$\text{O}_2$	25.0	2.9	10.1	14.5	5.1	13.8	33.7	5/9*
47-A	402 Lot 2	8.8	1.3	Chem.	4/4	3-5	4	$\text{O}_2$	130.0	2.3	30.1	9.4	3.3	8.9	9/10	
				Chem.	4/4	3-5	4	0.01% $\text{H}_3\text{PO}_4$	57.0	7.7	20.6	9.7	4.5	9.2	14.4	9/10
			Chem.	3/2	4	4	4	0.01% $\text{H}_3\text{PO}_4$	19.0	0.38	4.8	10.3	3.6	9.8	10/10	
			Std.	4/4	-	-	-	$\text{O}_2$	6.8	0.42	2.01	15.2	3.9	14.7	26.3	9/10
48-A	402 Lot 2	9.1	1.5	Std.-Chem.	4/3	3-5	3	$\text{O}_2$	6.2	0.42	2.34	15.1	6.5	14.2	42.5	8/10
				Chem.-Std.	3/4	3-5	3	$\text{O}_2$	86.0	0.23	10.0	12.0	6.3	11.0	21.0	10/10
			Chem.	4/4	3-5	3	3	$\text{O}_2$	16.0	2.4	7.8	8.6	4.8	3.1	15.6	10/10
			Std.	4/4	-	-	-	$\text{O}_2$	3.2	1.0	2.0	15.8	3.2	15.6	21.5	9/10
52-A	402 Lot 2	9.3	1.4	Std.	4/4	3-	-	$\text{O}_2$	9.3	2.0	4.3	16.4	2.8	15.1	19.5	8/10
				Chem.	4/4	2-3	4	$\text{O}_2$	34.0	8.2	18.5	10.8	3.3	10.4	10.4	9/12
			Chem.	3/2	4	4	4	$\text{O}_2$	120.0	10.0	49.8	10.9	2.8	10.6	8.9	4/12
			Chem.	4/4	2-3	4	4	$\text{O}_2$	82.0	4.9	39.1	10.2	3.2	9.9	8.5	9/12
			Chem.	3/2	2-3	4	4	$\text{O}_2$	100.0	10.0	56.3	10.1	3.6	9.7	11.2	4/12

\* Batch 46-D was dropped after dipping in silver.

TABLE 4B Task A, Activity 5.5

CHANGE OF L, C, D, VALUES OF CHEMICALLY IMPREGNATED CAPACITORS ON AGING AND LIFE TESTING

Batch No.	Preparation				No. of Failures			Measurements at 35 Volts								No. Hrs. on Life Test	
	Method of Impreg.	Cycle No.	Time-Mins.		Reformation Electrolyte	In Process	On Aging	On L.T.	After Canning		After Aging		After Life Test				
			Dip	Dry					I <sub>r</sub> -µa	C-µf	D.F.%	I <sub>r</sub> -µa	C-µf	D.F.%	I <sub>r</sub> -µa		C-µf
43-A B C D	Chem.	4/4	2	2	O <sub>2</sub>	2/10	8/8	-	-	12.8	1.7	20.2	-	-	-	-	Not on Life Test
		4/4	2	2	0.01% H <sub>3</sub> PO <sub>4</sub>	2/12	9/10	No Test	-	19.7	3.2	33.5	14.0	-	-	-	
		3/2	2	2	0.01% H <sub>3</sub> PO <sub>4</sub>	2/10	8/8	-	-	20.2	4.7	20.5	-	-	-	-	
	Std.	4/4	-	-	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	0/10	No Test	-	1.6	13.3	1.7	27.9	-	-	-	
44-A B C D	Chem.	4/4	2-3	4	O <sub>2</sub>	1/10	1/9	8/8	100	3.6	9.8	3.2	4.6	9.7	3.3	-	1003
		4/4	2-3	4	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	1/10	9/9	100	6.3	10.1	4.7	2.1	10.0	4.8	-	
		3/2	2-3	4	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	0/10	9/10	90	1.9	10.0	5.3	0.4	9.9	5.3	41.0	
	Std.	4/4	-	-	O <sub>2</sub>	1/10	0/9	5/9	56	2.5	13.9	3.1	2.5	13.3	2.9	22.0	
45-A B C D	Chem.	4/4	3-5	4	O <sub>2</sub>	1/10	0/9	8/9	89	19.3	9.3	5.1	4.1	9.1	5.3	98.0	300
		4/4	3-5	4	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	0/10	10/10	100	39.9	7.0	30.4	16.4	6.7	31.1	-	
		3/2	3-5	4	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	1/10	9/9	100	7.2	8.7	14.3	3.9	8.9	13.6	-	
	Std.	4/4	-	-	O <sub>2</sub>	0/10	0/10	1/10	10	0.46	14.0	3.7	0.4	13.1	3.9	1.29	
46-A C D	Chem.	4/4	3-5	4	O <sub>2</sub>	1/8	0/7	7/7	100	4.3	9.3	3.6	2.0	9.1	3.4	-	900
		3/2	3-5	4	O <sub>2</sub>	1/9	2/8	3/6	50	10.3	9.5	3.1	3.5	9.4	2.9	2.90	
		4/4	-	-	O <sub>2</sub>	4/9*	0/5	4/5	80	10.1	14.5	5.1	6.9	13.8	4.6	3.7	
	Std.	4/4	-	-	O <sub>2</sub>	1/10	0/9	9/9	100	30.1	9.4	3.3	12.1	9.4	4.2	-	
47-A B C D	Chem.	4/4	3-5	4	O <sub>2</sub>	1/10	0/9	9/9	100	20.6	9.7	4.5	14.7	9.5	4.7	-	954
		4/4	3-5	4	0.01% H <sub>3</sub> PO <sub>4</sub>	1/10	0/9	9/9	100	4.8	10.3	3.6	0.3	10.3	3.5	13.2	
		3/2	3-5	4	0.01% H <sub>3</sub> PO <sub>4</sub>	0/10	1/10	7/9	78	2.0	15.2	3.9	1.1	14.8	3.9	6.72	
	Std.	4/4	-	-	O <sub>2</sub>	1/10	0/9	2/9	22	2.0	15.8	3.2	1.3	15.4	3.1	3.2	
48-A B C D	Std.-Chem.	4/3	3-5	3	O <sub>2</sub>	2/10	3/8	4/5	80	2.3	15.1	6.5	0.5	14.9	5.1	0.45	254
	Chem.-Std.	3/4	3-5	3	O <sub>2</sub>	0/10	2/10	5/8	63	10.0	12.0	6.3	0.4	11.9	6.4	15.3	
	Chem.	4/4	3-5	3	O <sub>2</sub>	0/10	0/10	9/10	90	7.8	8.6	4.8	2.0	8.7	5.7	2.4	
	Std.	4/4	-	-	O <sub>2</sub>	1/10	4/9	3/5	60	2.0	15.8	3.2	1.3	15.4	3.1	3.2	
52-A B C D E	Std.	4/4	-	-	O <sub>2</sub>	2/10	4/8	No Test	No Test	4.3	16.4	2.8	4.7	15.8	2.6	-	Not on Life Test
	Chem.	4/4	2-3	4	O <sub>2</sub>	3/12	4/9			18.5	10.8	3.3	8.9	10.9	2.7	-	
	Chem.	3/2	2-3	4	O <sub>2</sub>	8/12	4/4			49.8	10.9	2.8	-	-	-	-	
	Chem.	4/4	2-3	4	O <sub>2</sub>	3/12	2/9			39.1	10.2	3.2	3.7	10.0	2.8	-	
	Chem.	3/2	2-3	4	O <sub>2</sub>	8/12	3/4			56.3	10.1	3.6	1.8	10.6	2.0	-	

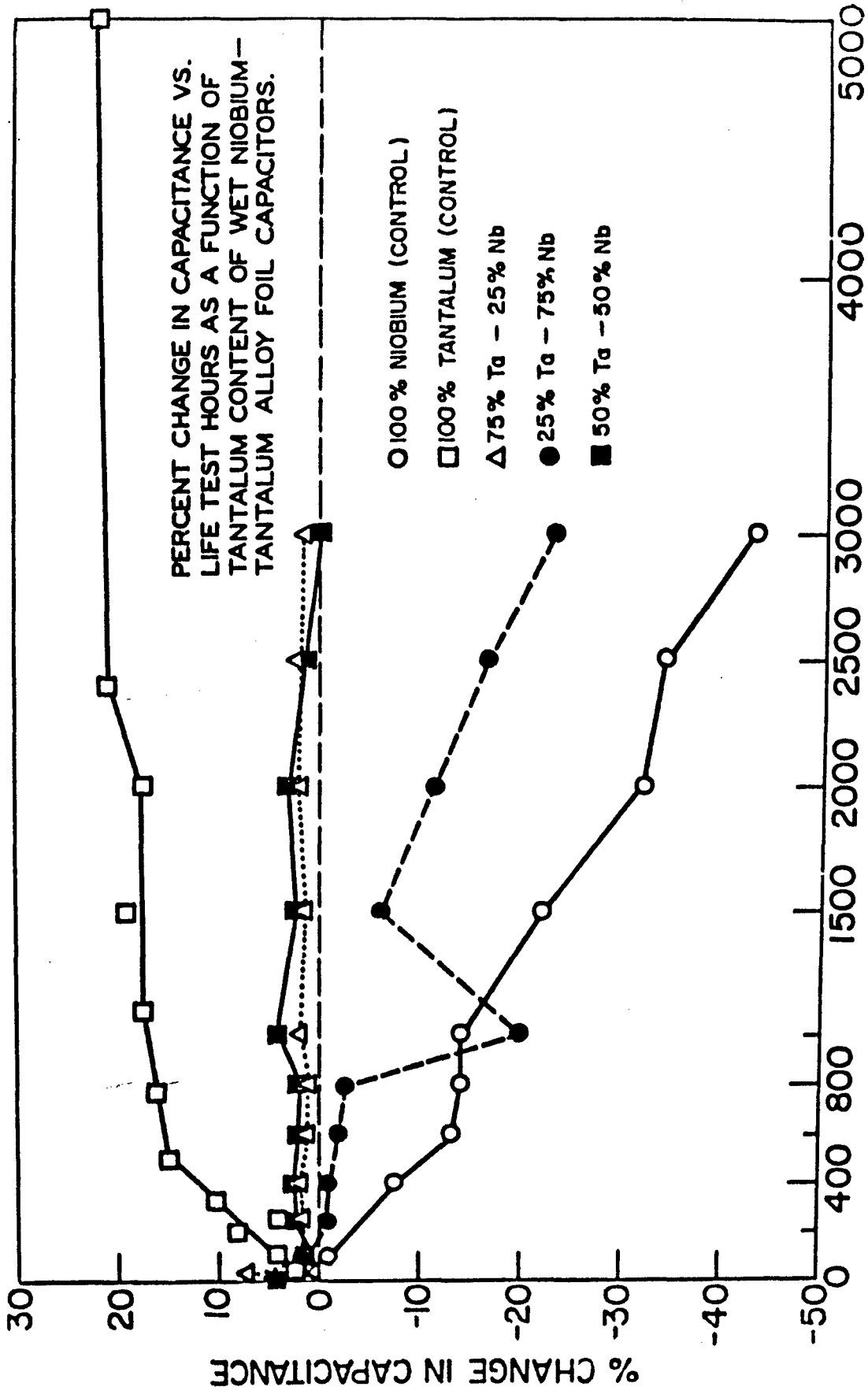
\* Accidentally dropped.

TABLE 5 Activity 10

NIOBIUM AND NIOBIUM-TANTALUM ALLOY POROUS ANODE CAPACITOR BATCHES,  
OF WET AND SOLID ELECTROLYTE TYPES, SUBMITTED TO THE BUREAU OF SHIPS

Batch No.	Description (Electrolytic)	Capacitor Type C $\mu$ f/V Volts	Can Size	Average Electrical Characteristics at Rated Voltage, 25°C		
				D.C. Leakage $\mu$ a	Capacitance $\mu$ f, 120 cps	D. Factor % 120 cps
1	Pure niobium solid	0.82/50	A	0.10	0.79	1.57
2	Pure niobium solid	5.6/35	B	0.55	5.8	2.38
3	Pure niobium solid	8.2/35	C	1.69	8.9	1.62
4	Pure niobium solid	10/35	C	0.85	10.3	1.53
5	Niobium-57% tantalum alloy solid	12/35	C	0.55	11.7	1.62
6	Niobium-57% tantalum alloy solid	8.2/50	C	2.19	8.6	3.43
7	Pure niobium solid	33/35	D	4.04	31.5	4.90
8	Niobium-57% tantalum alloy solid	39/35	D	2.11	38.6	5.16
9	Pure niobium porous anode wet	1.5/100	T-1	0.15	1.55	2.18
10	Niobium-81% tantalum alloy porous anode wet	2.5/100	T-1	0.068	2.38	2.67
11	Pure niobium porous anode wet	20/100	T-3	2.87	19.8	5.63
12	Niobium-81% tantalum alloy porous anode wet	22/100	T-3	1.37	21.3	7.44

Note: The maximum operating temperature on all batches, with the exception of batches 9 and 11, is +85°C, for these two, +65°C.



LIFE TEST (HOURS)  
FIG. 1



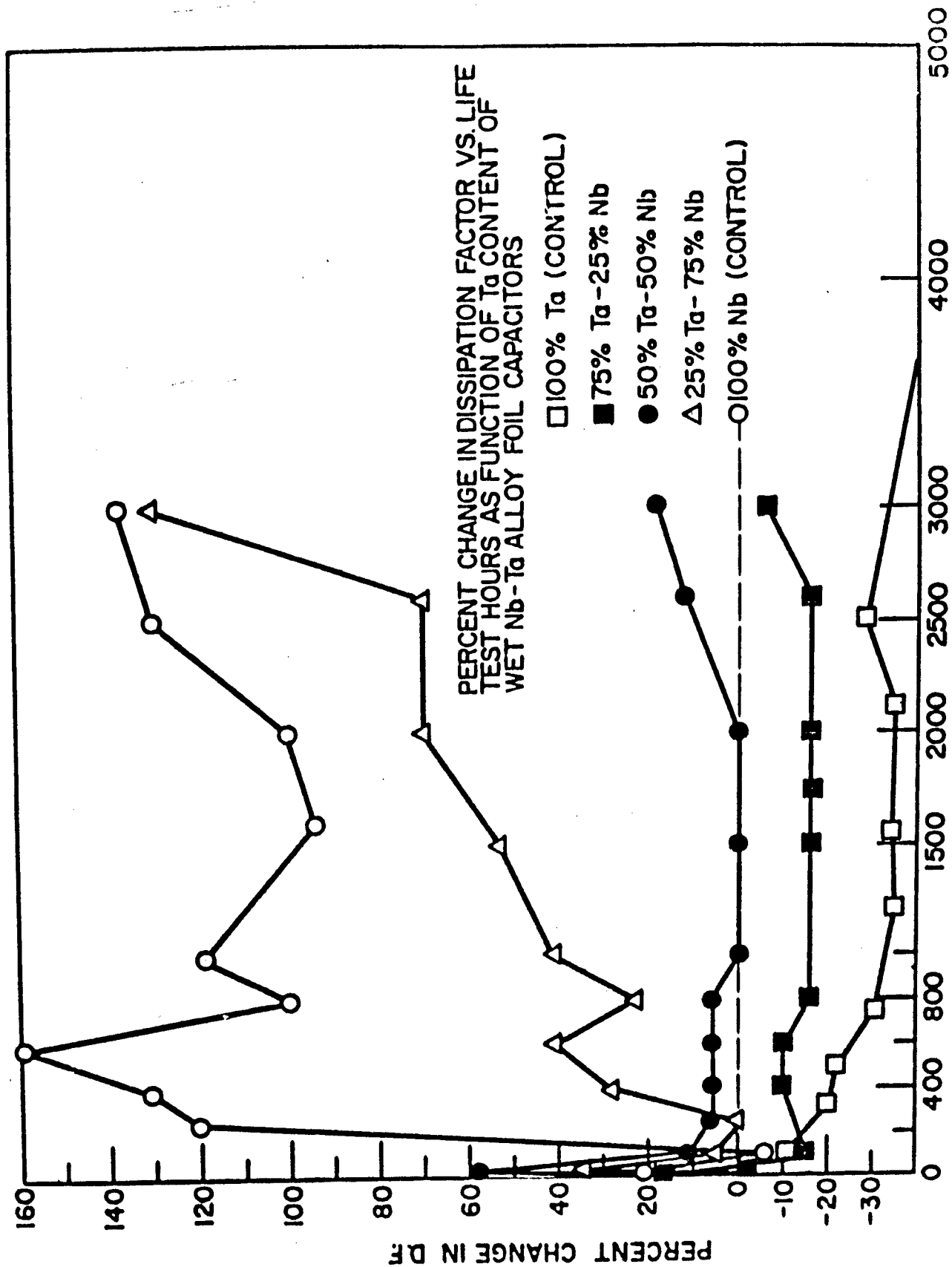


FIG. 2

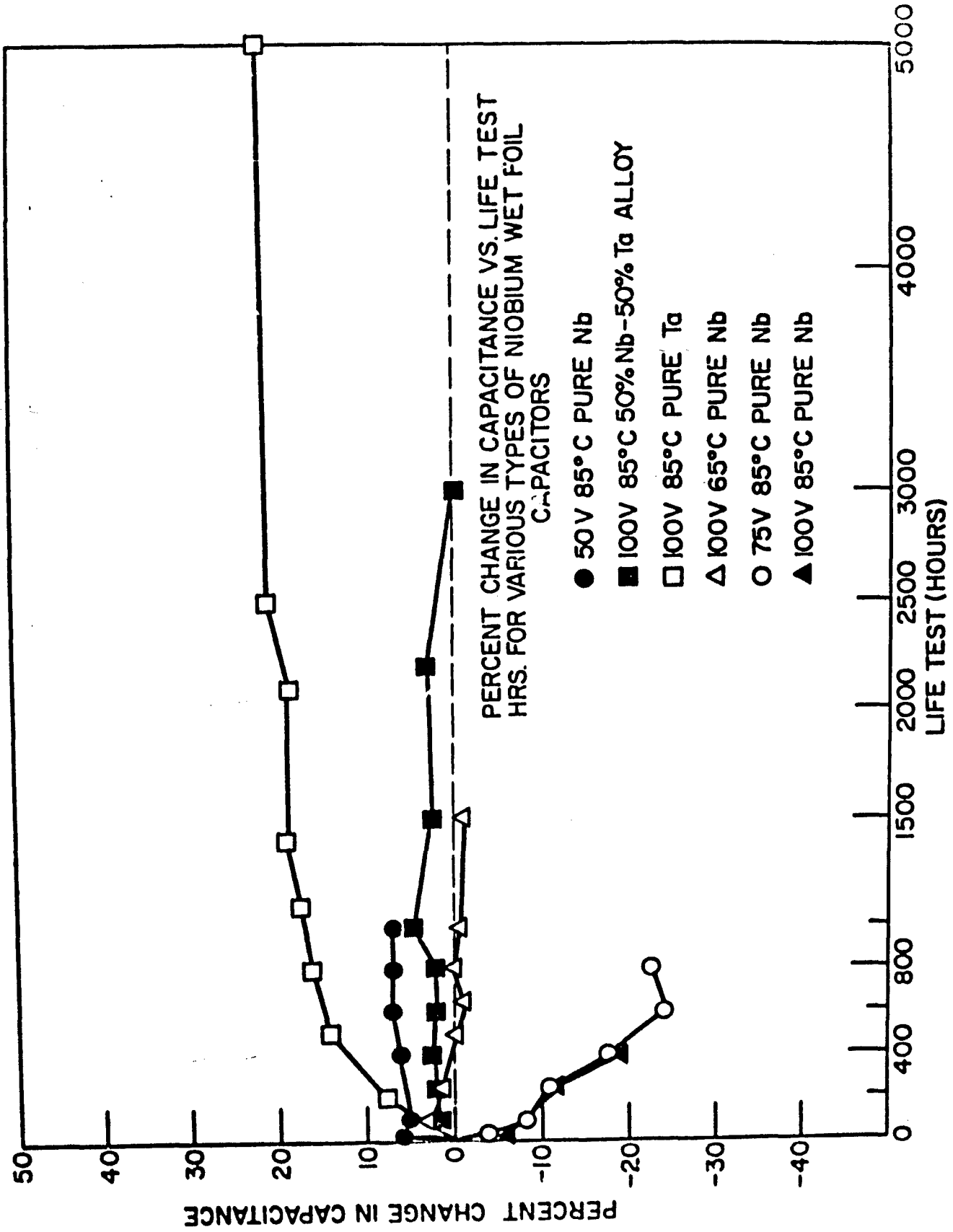


FIG. 3A

**PERCENT CHANGE IN DISSIPATION FACTOR VS. LIFE TEST HRS. FOR VARIOUS TYPES OF NIOBIUM WET FOIL CAPACITORS**

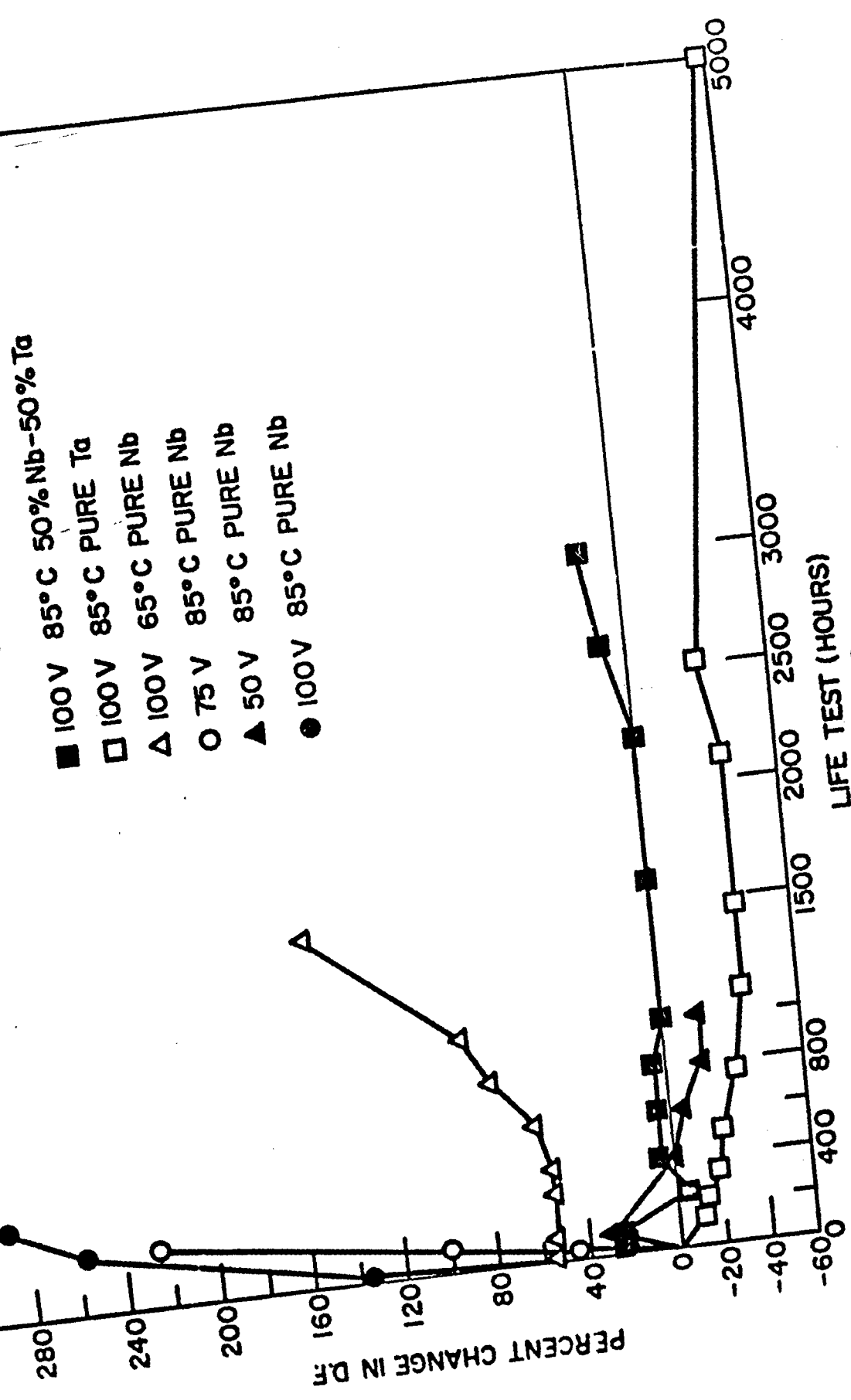


FIG. 3B

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