THE TANTALUM-CASED TANTALUM CAPACITOR

by

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Sprague Electric Company North Adams, Massachusetts To many of the engineers who have joined the ranks in electronics over the past 25 years, active components may seem to have all of the new developments and excitement. Many of these engineers feel that there is nothing new or progressive in the passive components field. Unfortunately for those who feel this way, they have limited themselves to too narrow a field of interest. One of the most interesting breakthroughs in passive components has occurred in the past two years. This is the tantalum-cased tantalum capacitor. What is a tantalum-cased tantalum? Let's go back and review electronic component history covering the past 25 years.

HISTORICAL

The first tantalum capacitors were sintered-pellet wet electrolytics. The foil tantalum capacitors and sintered-pellet solid-electrolyte tantalum capacitors were developed later. Application areas best suited for these various parts have been carved out and each of them has expanded through the years. However, at this time only the sintered-pellet wet electrolytic tantalum capacitor will be considered.

Sintered pellet liquid-electrolyte tantalum capacitors have evolved through numerous generations over approximately the past 25 years. These capacitors occupy their own unique position in the components field, especially when low leakage currents are a "must" circuit requirement. Usage of these capacitors, sometimes referred to as "wet-anode" or "wet-slug" capacitors, has continually and steadily increased as new developments have made them more versatile and reliable. The newest generation of parts to fill this need incorporates a radical change from the designs in the previous 25 years. This new development is the tantalum-cased tantalum capacitor. In this design, capacitors are encased in tantalum cases and have welded glass-to-metal hermetic seals. The cathode is now a gel rather than a liquid. This unique construction has a performance capability far beyond what was previously thought to be achievable.

The need for this newest design of capacitor can best be defined by outlining some of the problems which have plagued the industry in the use of silvercased wet slug capacitors. The problems which will be outlined did not, in general, occur with capacitors manufactured by Sprague Electric Company. However, because of the frequency of problems in other manufacturer's parts, NASA believed that a new generation of parts, made without silver, should be developed.

APPLICATION CONSTRAINTS OF OLDER DESIGN UNITS

The conventional wet slug tantalum capacitor is shown in Figure 1. It consists of a sintered pressed tantalum powder anode immersed in a suitable container containing a liquid or gelled electrolyte. The electrolyte completely permeates the porous sintered slug. All surfaces of the anode are oxidized. Thus the capacitor has a tantalum anode, tantalum pentoxide is the dielectric, and the electrolyte that surrounds and permeates the tantalum slug forms the cathode of the capacitor. The container into which this is placed is used to contain the electrolyte and also provides a suitable electrical connection to the cathode (electrolyte). Over the years, the container has been made of silver as the only reasonably successful material that could be used. The electrolyte is typically sulfuric acid. Therefore the container must be able to withstand the sulfuric acid without being consumed by the acid. A silver case only partially fits into this category. Silver does go into solution in sulfuric acid, primarily in the form of silver sulfate. Such silver in solution obviously has to come from the case. And its wall thickness is thus reduced.



Figure 1. Conventional wet slug tantalum capacitor.

The electrical limitations which are placed on silver-cased wet-slug tantalum capacitors, of necessity, are set to have a minimum effect on transferring excess silver from the case into solution or onto the anode. Since most electrolytic capacitors are used for dc filtering applications, it is obvious that the parts do not see a pure direct voltage but dc voltage with a superimposed alternating voltage. The prime function of the capacitor is to store up excess energy when the ac voltage wave is at its peak and to release this energy when the ac voltage wave is at its trough. Thus, it becomes obvious that to perform its function, the capacitor actually sees an ebb and flow or repetitive reversal of electric current. When the current is flowing into the anode, the electron flow in the capacitor is such as to hold the silver ions in the silver case. When the current is flowing out of the anode, then the electron flow is such that the silver ions from the case tend to go into solution in the sulfuric acid and, potentially, be electroplated onto the anode. If there is no alternating voltage, then the electric field of the direct voltage between the anode and the cathode will keep the silver ions in the silver case and not in solution. If there is no dc or ac voltage applied to the part, then silver will go into solution in the sulfuric acid until chemical equilibrium is attained.

Therefore, it can be seen that a wet slug capacitor, stored on the shelf, will have some silver in solution because of the inherent electrochemical reactions taking place. The silver in solution increases until chemical equilibrium has been attained in the electrochemical system. If pure dc is then applied to the capacitor (with no ac component), the silver ions in solution will be driven out of solution in the sulfuric acid and will be deposited back onto the silver case. If ac voltage is superimposed on the direct voltage, silver from the case will go into solution during one-half cycle of the ripple current.

During the second half-cycle, the silver will be redeposited on the silver case. Unfortunately, the silver ions do not necessarily redeposit back to their original location. Under these conditions there is a silver buildup elsewhere on the case.

Figure 2 is a magnified cross-section of a silver case showing where silver has been removed. The thickness of the silver can is obviously reduced at the pits. Figure 3 is another cross-section of a silver can in which the silver has been replated onto the can where the silver thickness had not been previously reduced. The silver that was plated back on appears as added thickness to the can. This is the type of condition that one expects when a part has been subjected to excess ripple current.



Figure 2. Magnified cross-section of a silver case showing where silver has been removed.



Figure 3. Cross section of a silver can in which the silver has been replated onto the can where the silver thickness has not been previously reduced.

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If reverse voltage is applied to a part, then the silver ions not only leave the silver can and go into solution, but they are subsequently attracted to the tantalum anode. They will find a weak spot in the tantalum pentoxide in which to attach themselves to a spot on the tantalum anode. Once the silver ions have been attached to a spot on the anode, further transfer of silver from the case to the anode will build or expand at that location. The type of growth that will occur from application of reverse voltage is shown by an enlarged cross-sectional view in Figure 4. This is commonly referred to as a "Christmas tree," so named because of the branch configuration that it takes. A "Christmas tree" of this type will continue to grow until it finally bridges the anode to the cathode. At that point a low impedance path exists to current flow and the part will behave as if it were short-circuited.

Another growth pattern caused by reverse voltage is shown in Figure 5. In this case the silver deposit tends to take a crystalline form.



Figure 4. Type of growth that will result from application of reverse voltage (enlarged cross sectional view).



Figure 5. Growth pattern resulting from application of reverse voltage in which the silver deposit in the case tends to take a crystalline form.

The silver from the electrolyte that is redeposited on the cathode can because of excess ripple or by a strong direct voltage of the proper polarity is shown in Figure 6. This is an enlarged view showing the silver crystals which have been redeposited on the inner surface of the can. These have been nicknamed "snowmen" by some of the engineers on NASA programs. Figure 7 is a further enlarged view of the crystals which have been deposited on the inside of some of these cases.

The foregoing discussion of silver migration outlines some of the problems which concerned Marshall Space Flight Center components personnel. Even though these problems were virtually unknown in Sprague silver-cased wet-slug capacitors, as already mentioned, the general existance of these problems in CLR-65 parts of other manufacturers clouded the acceptability of any CLR-65 for use in spacecraft. The application of silver-cased wet-slug capacitors is not always properly undertaken. And then the silver migration problems just



Figure 6. Silver from the electrolyte that is redeposited on the cathode can because of an excess ripple or by a strong direct voltage of the proper polarity.



Figure 7. Enlarged view of the silver crystals shown in Figure 6.

described can manifest themselves. Probably one of the most vexing problems to the space program has been how to cope with the long-time interval that exists from the time that parts are procured until the assemblies are used, i.e. the long-term storage of equipment on the shelf.

In many cases five or more years pass between the time that the equipment was manufactured and the time that it is used. With these problems to contend with, it became obvious that NASA needed a better capacitor to use in these types of applications. There are other capacitors which could be considered since the silver-cased wet-slug capacitors could experience silver migration problems. The other types of capacitors also have drawbacks. Solid tantalum capacitors have a catastrophic failure mode. Foil tantalum capacitors tend to be less effective in filtering action as well as being appreciably larger and heavier. Aluminum electrolytic capacitors have not been used because of a lack of hermetic seal and for other good reasons. Thus, the silver-cased tantalum capacitor, despite its faults, was still an excellent choice in most of these applications. These problems were outlined by Marshall Space Flight Center of the National Aeronautics and Space Administration to the Sprague Electric Company. The components manufacturer indicated that they already had a low priority in-house project which, if successful, would provide a solution to this problem. It was the same type of development which NASA engineers had contemplated as solving their problems. Based on the preliminary work that Sprague had done over a number of years and the requirements of NASA for a part to achieve these results at an early date, a contract was awarded by NASA to the Sprague Electric Company to expedite the development of a tantalum-cased tantalum capacitor.

TANTALUM-CASED TANTALUM CAPACITORS

The basic criteria which were established as goals for the tantalum-cased tantalum capacitor were simple but all inclusive. The part must be physically and electrically interchangeable with the parts already in use which were procured as MIL Style CL65, CLR65, and CLR67 parts. If the new design could be made completely interchangeable with the old parts, then any new production runs of equipment could use parts of the new design without any engineering redesign efforts. In many cases where a problem was known or suspected to exist, parts of the new design could be used for direct retrofit, again without engineering redesign efforts. Last, but by no means least, would be the expanded use of the part by other than NASA due to its interchangeability with Style CLR65 parts already designed into military and other critical applications. This universal applicability of the part would appreciably improve the availability of the part due to wider usage. These requirements were all met by the development of the Sprague Type 135D tantalum-cased tantalum capacitor. Figure 8 shows the similarity of appearance and physical size of a welded-tubulation, silver-cased wet slug capacitor and an all-welded, tantalum-cased tantalum capacitor.



Figure 8. Comparison of welded-tubulation silver-cased cylindrical capacitor with all-welded tantalum-cased cylindrical capacitor.

The real keys to the successful development of the tantalum-cased tantalum capacitor were the development of a high-capacitance tantalum cathode contact surface on the inside of the tantalum case, as well as the welded closure between the glass-to-metal seal and the tantalum case. These were the major obstacles that had to be overcome to have a ''one-for-one'' replacement for silver-cased, wet-slug tantalum capacitors.

ATTRIBUTES ACHIEVED WITH THE SPRAGUE TYPE 135D

The Sprague Type 135D tantalum-cased tantalum capacitors shown in the photograph of Figure 9 are currently available in four case sizes. They are capable of meeting all of the physical and electrical requirements of the parts they are designed to replace.



Figure 9. T1, T2, T3, and T4 tantalum-cased wet slug tantalum capacitors.

SHOCK, VIBRATION, AND THERMAL SHOCK

The highly successful basic shock and vibration resistance construction for wet-slug capacitors developed by Sprague and successfully used for many years has been incorporated in the Type 135D as shown in Figure 10. Figure 11 is a cross-section photo of this construction. The PTFE 'spider' supporting the lower end of the slug is visible. The PTFE bung supports the top of the slug. It is in compression under the glass-to-metal seal which is welded in place. The "flow" of the PTFE bung over the top edge of the slug due to the compression assembly is readily visible. Incidentally, the sintered tantalum cathode liner is also visible along the sides of the case. Thus, the Type 135D will withstand 80 g vibration or 0.06 degree double amplitude vibration, whichever is less, over the range from 10 to 2000 Hz for 3 h in each of the two axes, axial and radial. This is appreciably more than the 20 g maximum vibration capability of conventional wet-slug tantalum capacitors with anodes which are inadequately supported. In addition to the ability of the parts to withstand 80 g vibration, a Type 135D capacitor will also withstand 100 g, 6 ms saw-tooth shock requirements. The requirements of MIL-STD-202, Method 213 are easily met. This combination of an all-welded case construction and the well-designed vibration support results in capacitors capable of withstanding far more than the thermal shock requirements of MIL-STD-202, Method 107.



Figure 10. Typical cross-section of all-welded tantalum-cased cylindrical wet-slug tantalum capacitor (Sprague type 135D).



Figure 11. Cross section photo of the highly successful basic shock and vibration resistance construction for wet slug capacitors developed by Sprague.

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TEMPERATURE STABILITY AND CAPACITANCE RATIO

Figure 12 shows the results of conducting the temperature stability test requirements of MIL-C-39006. This family of curves is for four ratings in the T3 case size. These curves compare very favorably with the parts they are intended to replace. It will be noted that the high capacitance-low voltage rated parts experience the most change. The vertical bars at each measurement temperature indicate the range of values that existed for the entire group of parts tested while the line connects the median values. Typical capacitance ratios versus temperature for a larger number of ratings in three case sizes are given in Figures 13(a), (b), and (c).



Figure 12. Results of conducting the temperature stability test requirements of MIL-C-39006.









Figure 13. Typical capacitance ratios versus temperature for a large number of ratings in three case sizes.





Figure 13. (Concluded)

TEMPERATURE RISE DUE TO RIPPLE CURRENT

A criterion of allowable temperature rise which results from ripple current has not been directly used in the past. In most types of capacitors, the maximum permissible temperature has usually been determined by the melting point of solder, the plastic point of plastic films, the boiling point of impregnant or electrolyte, etc. These factors are no longer as applicable for Type 135D capacitors as they have been for other parts. These capacitors are constructed of only four materials: tantalum, glass, PTFE, and sulfuric acid. Therefore, since there is no silver for silver migration and the capacitors are assembled by welding instead of soldering, it becomes possible to consider maximum temperature as the criterion for ripple current. With this in mind, a number of temperature rise versus rms ripple current curves were plotted. These tests were all made at ambient room temperature. The extreme values are plotted in Figure 14. It can be seen that a given temperature rise results from a lower ripple current at 120 Hz than at 40 kHz. This, of course, is caused by the decrease in equivalent series resistance (ESR) as frequency increases. Typical values of ESR as a function of frequency are given in Figure 15.

Evaluations of life as a function of applied ripple current are being made. At the present time, it appears that the prime consideration is the maximum temperature of the unit. A conservative temperature rise limit of 50°C over



Figure 14. Extreme value temperature rise versus rms ripple current curves.

ambient with a maximum of 125° C ambient temperature is currently used. This compares with a temperature rise limit of 5° C to 10° C with a maximum of 85° C or 125° C ambient temperature for currently made silver-case parts. Preliminary data indicate that a more realistic limit for the 135D will probably be 175° C or higher.

SURGE CURRENT CAPABILITIES

Earlier it was stated that filter capacitors in power supplies have limitations that must be met if a reasonable performance capability is to be achieved. Probably the most severe application is the input capacitor of a capacitor-input type of filter. This capacitor is subjected to severe surge currents as well as high ripple currents. A solid tantalum capacitor in this application tends to fail by short-circuiting without prior warning. A silver-case wet-slug capacitor is an improvement but has silver migration problems with high ripple currents.



Figure 15. Typical values of ESR as a function of frequency.

In the Type 135D capacitors, there is no silver present and silver migration is obviously no problem. It was believed desirable to evaluate their surge (inrush) current capability in this type of application. The circuit of Figure 16 was set up. The 100 000 μ F capacitor is a stacked-foil aluminum electrolytic design with a very low ESR (measured in milliohms). The total current-limiting



Figure 16. Timer using two 30 A mercury relays.

circuit resistance, including the fuse, is less than 0.3Ω . With this circuit, individual capacitors are subjected to more than 100-amp charge and discharge surge currents. The results of 100 000 charge/discharge cycles are shown in Figure 17. The vertical bars in the upper figure show the range of capacitance values for all the parts tested while the curve ties together the median values. After 100 000 surge-current cycles, typical capacitance values had only changed about 1.6 percent. The lower curve shows the average leakage current for the lot of parts tested as a function of the number of surge current cycles. It can be seen that the average leakage current decreased by an order of magnitude.



Figure 17. The results of 100 000 charge/discharge cycles.

LIFE TESTS

Of all of the testing and evaluation that needs to be performed on a new device, obviously life testing requires, by far, the most time. Therefore, during the early stages of evaluation, life test data will be less complete than other types of evaluation data. The 135D capacitor is no exception to this fact of life. At present, dc life tests beyond 10 000 h (approximately 14 mos) have been completed on a number of ratings. Typical of these are the data plotted in Figure 18. Note that the parts are extremely stable with time. The more stringent ripple current life tests have not reached the 10 000 h mark as yet. However, the preliminary data are most encouraging.



Figure 18. Plot of dc life tests.

CONCLUSION

The development program originally conceived by Sprague Electric and accelerated and expanded under the moral and financial support of the Marshall Space Flight Center of NASA has produced a new and superior capacitor. Tantalum-cased tantalum capacitors have already found acceptance by the military to upgrade the performance and reliability of critical electronic equipment. Type 135D capacitors are currently being evaluated for use in other life support and life critical applications. The wide applicability of these capacitors with their superior performance should make them the 'work-horse' of the next generation of equipment.

ACKNOWLEDGMENT

It is virtually impossible to identify all of the engineers, scientists, and skilled craftsmen who have contributed to the development of the Sprague Type 135D capacitor. Some of the solutions to problems encountered were the results of suggestions of specialists not directly involved in the program but who followed the program with great interest. To all of these many people, working in concert toward a single goal, goes the total credit for an outstanding accomplishment.

Very important recognition goes to the Marshall Space Flight Center of the National Aeronautics and Space Administration for its financial assistance on this project during the last 3 years of the development. Equally as important was the moral support and probing interest of Dr. Holladay, Messrs. Hamiter and Nowakowski, and their support staffs at Marshall Space Flight Center. It was NASA's urgent need for a part of this type that accelerated the Sprague ''in-house'' efforts which culminated in the development and manufacture of the Type 135D tantalum-cased tantalum capacitor for aerospace and military electronics as well as other high reliability applications.