Technical Memorandum 33-588

Evaluation of New Plastic Compression (Ziegler)
Type of Seals for Long-Life Planetary Batteries

H. A. Frank

February 1, 1973
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PREFACE

The work described in this document was performed by the Guidance and Control Division of the Jet Propulsion Laboratory.
ACKNOWLEDGMENT

The author would like to acknowledge the assistance of the Bell Telephone Laboratories and in particular Mr. E. J. McHenry for supplying all the necessary technical information on the Ziegler seals for this evaluation program. In addition the author would like to acknowledge the assistance of Mr. Ralph Renner, JPL Fabrication Section, for design of the seals, and Mr. Don Lawson, JPL Astrionics Research Section, for conducting the helium leak testing.
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ABSTRACT

A program was initiated to develop improved types of terminal seals for aerospace Ni-Cd batteries. The approach used has not involved attempts, such as employed elsewhere, to improve the ceramic-to-metal seal that is now extensively employed for this application. Rather the approach has been directed toward the development and evaluation of new types of seals. Of prime interest in this initial investigation has been the "Ziegler" type of compression seal and in particular the injection molded version developed by the Bell Telephone Laboratories (BTL). A number of these units were designed, fabricated, and evaluated on an accelerated life test under a simulated battery environment. Results have shown that there are no major problems involved in scaling up the BTL small-size (5-amp) seal to a larger-size (up to 50-amp) seal suitable for most JPL flight batteries. Five out of five such seals successfully completed over 10 months of continuous thermal cycling (2-h cycle from -40°C to +71.1°C without developing any leaks greater than $1.8 \times 10^{-9}$ atm-cm$^3$-He/s.
I. INTRODUCTION

Leaks are known to represent a threat to performance of sealed electrochemical cells because they permit loss of electrolyte that is essential for normal cell operation. The losses may occur in the form of liquid electrolyte and water vapor, as well as hydrogen and oxygen gases. In the case of sealed nickel-cadmium cells the leaks may also, because of loss of oxygen, result in a condition of capacity imbalance that may, under certain conditions, result in catastrophic failure. The threat of leaks is especially severe in cells that are intended for use in the aerospace environment wherein the losses of these components will be quite rapid and there is no means for returning them to the cell. Of particular concern are those cells that are intended for use on long duration planetary missions where even the smallest of leaks may endanger the spacecraft's power system and even jeopardize the mission.

In view of the Jet Propulsion Laboratory's (JPL's) responsibility for these missions and its awareness of these problems, the Laboratory has taken a number of precautionary measures to insure that its flight batteries will be sufficiently leak tight for the duration of their design lives. These measures may be divided into three general areas as described below.

The first is aimed at determining the maximum permissible leak rate of a cell in the aerospace environment consistent with its size and design life. This type of information is not generally available and is essential for the establishment of meaningful leak standards. The work has been carried out by correlating leak size with loss rates of these components and also determining the effect of these losses on electrical performance of various types and sizes of cells (Ref. 1). The second area is aimed at confirming leak specifications of flight-type cells that are delivered from various vendors. This has involved the conduct of a variety of leak detection and inspection tests including the phenolphthalein test, helium leak test,
microscopic examination, and X-ray examination (Ref. 2). These tests are performed on the cells as received, after environmental test, and before flight as required. The third area is aimed at reducing the probability of developing leaks in cells—especially those that are intended for long-term planetary missions. This work has involved the development and evaluation of new designs and materials for critical leak areas including terminal seals and the case to cover seals.

Most of the prior efforts in this third area were concerned with sealing Ag-Zn cells that by virtue of their high energy density were used quite extensively in Surveyor and Mariner missions. Noteworthy achievements in this area included development of improved cements for bonding the plastic cell cases and covers and in development of improved potting materials and techniques for sealing the cell terminals to the plastic cover assemblies (Ref. 3).

Current efforts in this third area have been concerned primarily with sealing Ni-Cd cells because these are known to yield a much longer electrochemical life than the Ag-Zn cells and are contemplated for use on the long-term planetary missions. Primary emphasis has been devoted to improving reliability of the Ni-Cd cell's terminal seals that have heretofore been of the ceramic-to-metal type and that have been shown both at JPL and elsewhere to be the cell's most vulnerable area regarding development of leaks. The JPL approach to this problem has not involved attempts, such as employed by other organizations, to improve the existing ceramic-to-metal seal by use of new materials and designs. Rather the approach has been to develop and/or evaluate entirely new types of seals that are not subject to the same severe problems associated with ceramic-to-metal seals. Of primary interest in this regard has been a new compression-type seal that has been under development by the Bell Telephone Laboratories (BTL) for use in Ni-Cd batteries for Bell System service. This type of seal is referred to as the "Ziegler" seal in honor of its inventor, A. W. Ziegler (Refs. 4, 5, 6, and 7). Attractiveness of this new seal is based primarily on the fact that it can be made of much more inert materials and does not require the critical fabrication and assembly procedures required for the existing ceramic-to-metal type. This applies especially to the new injection molded Ziegler seals described by McHenry (Ref. 6). Consequently, the Ziegler seals should prove much more reliable than the ceramic-to-metal type.
The following sections of this document contain detailed descriptions of this seal, review its development at BTL, and give results of its recent evaluation at JPL.

II. DESCRIPTION OF ZIEGLER SEAL

The Ziegler Seal, like the ceramic-to-metal and other types of seals, serves a dual function. First it is used to hermetically seal the lead-in connections or terminals of electrical devices. Secondly, it is used to electrically insulate these terminals from one another and also from the case or chassis of the electrical device. In the application of interest the seals are used to prevent leaks in the terminals of Ni-Cd cells and insulate these terminals from the metallic Ni-Cd case.

The Ziegler seal is classified as a compression-type seal in that it relies, like other seals of this type, on the mechanical compression of a plastic material against rigid surfaces to perform its functions. As such, its effectiveness is dependent on several mechanical design factors consisting of the magnitude of the compressive force against the rigid surfaces, the maintenance of this force, and a large contact area between these surfaces and the plastic. In addition, the effectiveness of the seal is dependent on several properties of the plastic including a high modulus of elasticity (with a desired modulus near $1.7237 \times 10^9$ N/m$^2$ in tension), a high shear strength (as shown by a compressive strength near $3.45 \times 10^8$ N/m$^2$), a low rate of stress relaxation (less than 20% in 10 years) and good machinability. Furthermore, the effectiveness of the seal is dependent on its use of plastics with low permeability to battery gases (hydrogen, oxygen, and water vapor) and stability of both plastic and metal components in the alkaline battery environment.

To clarify the discussions that follow, it would be well at this point to briefly define three variations of the so called "Ziegler" seal in accordance with McHenry (Ref. 6). The first is designated as the "standard" version and refers to the original seal that was developed and patented by A. W. Ziegler of BTL in 1963. This is a machined form of the seal that was evaluated previously by both BTL and JPL. The second is designated as the "injection molded" version that was subsequently developed by BTL and has
currently been under investigation at both BTL and JPL. This version is essentially the same as the standard but is made, as implied by its name, by an injection molding rather than a machining operation. The third is designated as the "multiple-crimp" version that was recently developed by BTL and is described in one of their recent patents (Ref. 8). This may be made by either the machining or injection molding process and is intended primarily for installation in cylindrical cells. Because of its recent development the multiple crimp seal has not been evaluated yet at JPL.

A cross-sectional view of the standard Ziegler seal is given in Fig. 1. This is comprised of three parts consisting of a metallic lead in connection or terminal rod (A), a plastic dielectric bushing (B), and a metallic barrel or collar (C). The terminal rod is made by machining bar stock of a suitable metal to the appropriate diameter for the given application. For applications requiring very small diameters the terminal may be made simply by cutting segments of smooth drawn wire that are free of longitudinal grooves. The bushing is made by machining bar stock of a suitable dielectric material. The inside of the bushing is drilled through to accommodate the rod and its outside is carefully threaded as described below. The barrel is made by drilling through a length of bar stock of suitable metal and then carefully threading its inside to conform to the threads of the bushing.

The assembly is installed on a Ni-Cd cell by first welding or brazing the barrel to the cell cover. Next, the terminal rod is passed through the barrel and the bushing is slipped on to the terminal rod and threaded into the barrel. The final step involves crimping the barrel with the aid of a specially designed compression tool in a hydraulic press. Because of the interengagement of threads of barrel and bushing, the latter is prevented from expanding in the axial direction during this operation. As a result this final operation places the bushing under a high state of compression which, as noted above, effects the seal.

A special requirement of this standard Ziegler seal is extremely close mating of the threads of its bushing and barrel. Required tolerances can seldom if ever be met by application of commercial threads as these contain sharp crests and roots that are exceedingly difficult to match, and result in helical leakage paths. Reliable results have been obtained only by application of the specialized Whitworth-type threads that feature rounded roots and
crests, which are much easier to match. These threads must be machined with great precision to avoid burrs that could also result in helical leakage paths in the plastic during the assembly operation. The task of machining these threads is therefore the most critical (and also the most time consuming) of all operations involved in fabrication of the standard seal.

Pure nickel is preferably employed as the material of construction for the terminal rod and barrel because of its known stability in the corrosive battery environment. Kel-F has been found to serve well as the material of construction for the bushing because it is also resistant to the battery environment, can be readily machined, and has most of the other desired physical properties listed above. Alternate plastics that have been considered but not yet thoroughly examined for this application include Teflon, polypropylene, nylon, and high-density polyethylene.

The injection molded Ziegler seal is very similar to the standard seal in that the former has the same overall configuration and operates on the same principles as the latter. The only major difference is in the method of incorporating the dielectric bushing material inside the barrel. In this case the material is introduced by injection molding rather than by the machining and threading operations as in the case of the standard seal. The first step in the fabrication process involves machining of the barrel from bar stock. This operation is much simpler than in the case of the standard seal in that it merely involves drilling and then threading the bar stock with a conventional tap such as an 8-32 tap and without rigid tolerances. The next step involves installation of the barrel and terminal rod in a specially designed mold that positions the terminal rod in the center of the barrel. At this point the assembly is placed in an injection molding machine and the annular space is filled with the appropriate polymeric material. Next the barrel assembly is welded or brazed to the cell cover. This operation must be carried out slowly and with adequate heat sinking to avoid damage to the plastic. Finally the barrel is crimped with a specially designed crimping tool as above. An alternate procedure is to carry out the welding or brazing step before the injection molding step. This procedure is preferable in that it does not require the use of heat sinks and reduces time requirements for welding or brazing.
Most of the seals that have been developed to date have employed nylon as the polymeric material primarily because it can be readily injection molded and appears to meet most of the mechanical requirements. This material is not, however, necessarily the optimum because it can react slowly inside the alkaline cell environment (Ref. 9). For this reason some attention has also been focused on alternate polymers that can be injection molded and are more resistant to the corrosive cell environment. Among these materials are polypropylene, Teflon, Kel-F, and Kynar.

The multiple crimp seal is basically the same as the two above types of Ziegler seals in that it is made from the same materials and operates on similar principles as the above types. The unique features of this version are that it is crimped in several rather than one location and it is specially designed for internal installation especially in cylindrical cells. The former feature provides additional insurance against development of leaks and the latter reduces the size penalty associated with the above types of seals and thereby permits development of very compact cell designs. A schematic diagram of the multiple crimp seal installed in a cylindrical cell is given in Fig. 2. The seal is comprised of an outer metal tube, an inner plastic material, and a centrally located terminal rod or wire as in the above seals. The simplest manner of assembly involves merely insertion of a plastic tube, with centrally located terminal rod, inside the outer metal tube and then crimping. Alternatively the seal may be injection molded, as above, and then crimped. In either case the assembly is installed in the cell as shown in Fig. 2 and the outer metal tube brazed to the cell cover.

III. JPL EVALUATION

Initial interest in the Ziegler seals at JPL occurred in 1967 when the Laboratory first became aware of their development at BTL and decided to evaluate them on contract with Texas Instruments. This initial involvement with the seals was rather short lived, however, as it was terminated with the completion of the above contract in 1969. Renewed interest occurred in 1971, however, when the Laboratory decided to evaluate improved versions of these seals under an internal program. This latter effort has been continued until the present time and is described in detail herein.
A. Texas Instrument Program

In 1967, JPL initiated a contract to develop a planetary-lander-type battery that was to be designed to withstand high levels of shock, acceleration, and vibration and also be capable of being heat sterilized. This was the "Heat Sterilizable and Impact Resistant Ni-Cd Battery" program that was awarded to Texas Instruments (TI) (Ref. 10). Preliminary design work on this program revealed that one critical problem area with such a battery would be that of obtaining terminal seals of adequate strength and flexibility to withstand these severe environmental conditions. Glass-to-metal seals were deemed inadequate because of their known fragility and slow reaction of the glass component with KOH solution. Ceramic-to-metal seals appeared to be promising at first in that they were shown to meet the mechanical requirements. These were ultimately ruled out, however, because the braze alloys in their ceramic-to-metal and metal-to-metal joints were also found to be subject to attack by KOH solution. The new compression-type Ziegler seal, then under development at BTL, appeared to offer much more promise than either of the above in that it contained no brittle members and all of its components were known to be quite stable in KOH solution. On this basis a significant effort of this program was placed on development and evaluation of the Ziegler seal. This was the standard version of this seal as described above and was composed of a stainless steel barrel, a Kel-F bushing, and a nickel terminal rod. Polypropylene was also examined as an alternate bushing material.

Results of the seal development portion of this program were encouraging from one point of view but yet quite discouraging from another. The encouraging result was that the seals were found to be quite effective in providing leak-free operation (with leak rate less than 10^{-10} atm-cm^{3}-He/s) for conditions that did not involve sterilization. The discouraging result was that none of the seals could be made to withstand the conditions of sterilization. Regardless of whether the seals were made with Kel-F or polypropylene or the manner in which they were assembled and crimped, all seals were found to develop gross leaks after being subjected to sterilization. The problem was found to be associated with distortion of the plastic bushing material upon exposure to sterilization conditions: 135°C for 72 h. This distortion released the normally high compressive forces within the bushing and permitted
development of helical leakage paths along its threaded perimeter. It was speculated that the problem could be solved by use of a more temperature resistant polymer (such as polyphenylene oxide) but there was insufficient time-to-demonstrate-this-point.

B. **Internal Program**

The negative results regarding capability of the Ziegler seals to withstand sterilization did not necessarily detract from JPL's overall interest in these seals. Contrarily, JPL's interest remained at a high level for several reasons. First, it had been demonstrated on the above program that the seals were indeed quite effective in providing leak-free operation of cells that were not subject to sterilization. This fact was further substantiated by the independent findings of BTL that were presented in a NASA "Battery Workshop" (Ref. 5) and by personal communication (Ref. 11). Next, JPL was cognizant of the fact that it had several forthcoming "flyby", "probe", and orbiting type of planetary missions in which sterilization was not a requirement and wherein the seals might indeed prove advantageous. Finally, JPL was aware of the many inherent weaknesses of the existing ceramic-to-metal seals and received reports from time to time that many of these did indeed develop leaks (Refs. 6, 12, 13, and 14).

After completion of the above program, JPL therefore remained in close contact with BTL to follow their new developments with these seals. Of special interest during this period was BTL's development of the injection molded seal as described previously. This version was obviously much simpler to fabricate than the standard version in that it did not require the intricate manual machining and assembly operations required of the "standard" version. As such, the injection molded version appeared to offer not only lower cost (which was a major goal at BTL) but, more importantly, even greater reliability than that of the standard version.

On this basis JPL initiated in 1971 an internal program to evaluate and qualify the injection molded seal for flight. Highlights of this continuing evaluation program are described below.

1. **Objectives and Approach.** The overall goal of this effort has been to develop improved terminal seals that will permit reliable and leak-free operation of sealed cells in the space environment for periods up to
12 years. The specific objective of this phase has been to evaluate for this purpose the compression-type Ziegler seal and in particular the injection molded version thereof. The approach has initially involved fabrication of a limited number of these new seals and the conduct of an accelerated life test in simulated alkaline cells. This will be followed by fabrication of additional units, installation of these on actual aerospace-type cells, and finally the conduct of performance tests on these cells under simulated aerospace missions. For comparative purposes, the latter tests will also be run with additional aerospace cells that employ the existing ceramic-to-metal seals and improved versions thereof.

2. **Design.** To initiate the program in an expeditious and efficient manner it was at first deemed advisable to procure the injection molded seals directly from BTL rather than to develop them in house. This approach had to be abandoned, however, when it was found that BTL was legally not allowed to sell these units and that furthermore they were designed for somewhat lower currents (near 1 A) than were required for JPL cells (20 to 50 A). Since there was no other alternative, JPL proceeded to design and fabricate the seals on its own.

Figures 3 and 4 give details of the JPL version of the injection molded seal. Criteria for this design were based in part on information supplied by BTL on their smaller seals and in part on information obtained on the larger seals in the TI program (Ref. 10). Diameter of the centrally located conducting wire was selected to be adequate to limit voltage drop to low levels. Calculated voltage drops per terminal with an assumed length of 4.0 cm and the use of pure nickel were 4.6 mV at 10 A, 9.2 mV at 20 A and 23.0 mV at 50 A. Overall configuration of the barrel assembly, including the type of internal thread, was in accord with the BTL design. This part was designed with an integral disc assembly on one end to facilitate installation on the cell cover. Wall thickness and length of the barrel were in accord with the larger TI design. In accord with BTL recommendations, the material of construction for the barrel-disc assembly was selected as stainless type 304-L, whereas material of construction for the central conducting wire was selected as pure nickel. Nylon 6-6 was selected as material of construction for the bushing for this initial version because it was known that this material could be readily injection molded and would meet the mechanical requirements.
This choice was made with full cognizance of the availability of materials such as Teflon, Kel-F, and polypropylene, which would meet the mechanical requirements and offer more chemical stability than nylon in the battery environment. These latter materials were ruled out at this stage however because of uncertainties regarding their suitability for injection molding. These materials would be examined for this application at a later date when more information would be obtained on details for injection molding them.

Figure 5 gives details of the crimping tool that was used to compress the barrel portion of the seal. Design of this tool was based primarily on that of a similar one used by BTL to compress their smaller seal. The only major difference was in the diameter of the center hole, which establishes the degree of compression. In this case, the diameter was selected as 0.991 cm so that the barrel, with an original diameter of 1.051 cm, would be compressed 0.061 cm. This degree of compression was approximately proportional to that employed by BTL, i.e., 0.046 cm compression on the barrel with an original diameter of 0.635 cm. The material of construction of this tool was selected as "Graph-Mo" steel rather than "Ketos" steel as employed by BTL. This decision was based on the fact that "Graph-Mo" is as strong but yet not as brittle as "Ketos" and there was less chance that the tool might be damaged in use.

3. Fabrication. Since JPL had all the necessary capability and facilities to machine and injection mold the seals, it was at first planned to carry out all the fabrication in house. Subsequent investigation, however, revealed a local vendor specializing in the fabrication of similar components who could most likely carry out the work in a more efficient manner than JPL. On this basis an order was placed with this vendor for fabrication of a limited number, 12, of the injection molded seals. The design of the compression tool was not finalized at the time of this order and was subsequently fabricated by JPL's Fabrication Section.

Several types of inspections were carried out on the seals as received from the vendor. The first consisted of visual examination and measurement of all external dimensions wherein it was found that they were all quite uniform and conformed to the specified tolerances. The second inspection involved sectioning of one unit to examine its internal construction. This revealed two irregularities as follows. First it was noted that the terminal
rod contained a slight knurl around its center portion about 0.635 cm in length. Next there were noted to be two small voids of about 0.158-cm diam in the nylon bushing. When asked to explain the presence of the knurl the vendor replied that his machinist had arbitrarily applied it so that the terminal rod would be held more securely in place. This "mistake" was dismissed in that it was not deemed detrimental and might even help improve performance of the seal. When asked to explain the occurrence of the voids, the vendor replied that the first of a group of items to be injection molded often times contains voids and the particular seal that had been sectioned was undoubtedly the first seal to be placed in the injection molding machine. To confirm this point a few more seals were sectioned and subjected to thorough examination. These were all found to be free of voids so that the vendor's explanation appeared to be valid. As explained in the next section an attempt was also made to detect voids in the remaining samples by X-ray inspections. These efforts were found to be unsuccessful however due to excessive wall thickness of the barrel assembly. At this point the sectioned samples (see Fig. 6) were set aside for additional tests and demonstration purposes and the remaining five units were installed in simulated cells as described below.

To prepare the seals for subsequent test and evaluation, the seals were installed in simulated alkaline cell assemblies as shown in Figs. 7 and 8. These assemblies were prepared by first locating some empty cell cases and covers from a prior program. These were 304-L stainless steel cases and covers for 5-Ah NiCd cells with the indicated dimensions as shown in Fig. 7. A small 0.635-cm hole was cut in the side of each case and a seal was then positioned over each hole and welded to the side of the case as shown. The welding operation was carried out quite slowly and with a block of aluminum inside the cell case to serve as a heat sink. Next a small, 0.318-cm-diam steel tube was welded to each cover to serve as a fill point. Finally the covers were welded to each case and Swagelock fittings and caps were installed on the ends of the tubes as shown in Fig. 8.

At this point the assemblies were given a preliminary "bubble"-type leak test to establish the presence of any gross leaks that might have resulted from faulty machining or welding operations. This involved application of 0.7 kg/cm² of air inside the assemblies and immersion of each inside a water bath to check for leaks. Results revealed that all of the weld areas were
apparently leak tight but that all of the seals were not. This result was not unexpected, however, because the seals had not yet been subjected to the crimping operation.

Finally the seals were crimped by inserting the barrel portion of each in the compression tool and the application of 15,800 kg in a hydraulic press. The seals were then leak tested again as above and found to be leak free, at least on the basis of the bubble test.

4. **Test.** The first formal test on the assemblies consisted of measuring their helium leak rates on a Veeco Model MS-9 Leak Detector. The tests were carried out by connecting the stainless steel tubes to the detector via an adapter and then surrounding the assembly with a plastic bag filled with helium. In this manner, the helium would pass through the leak area, into the cell assembly, and then into the detector. Results for each of the assemblies revealed leak rates of less than $1.8 \times 10^{-9}$ atm-cm$^3$-He/s, which is the lowest detectable limit of the device. These results signified that the leak rates of each of these seals was no greater than and possibly less than the above value.

Next, the units were subjected to a series of X-ray tests to establish whether or not it was possible to detect the presence of additional voids in the bushings and also to examine internal dimensional changes of the barrel. The units were examined in different orientations and at different radiation levels and times with a Norelco MG 150K X-ray unit. Typical views of one such assembly before and after compression and in the same orientation are given in Fig. 9. The change in internal dimensions of the barrel is clearly evident from these two crude photos. The changes could be determined quite accurately with suitable photographic enlargement techniques. The internal nylon bushing was not visible in Fig. 9 nor could this yet be seen with any degree of clarity in any of the other views. The thickness and density of the outer barrel were obviously too great to permit a view of the inner bushing material. Therefore it was not possible to detect the presence of voids or other low density inclusions in the bushing material.

At this point the assembly weights were taken in both the dry condition and after having added KOH solution (see Table 1). Next the assemblies were placed on an accelerated life test that had been previously shown to give reasonable estimates of expected seal life (Ref. 6). This test
consisted of continuous exposure of each assembly to a 2-h thermal cycle regime between the temperature limits of +71.1°C and -40°C. The work was accomplished by installing the assemblies in a Bemco Environmental Chamber (Model F100/350-8) that had been previously programmed to deliver the desired thermal cycles. Details of the thermal cycle are given in Fig. 10, which is a typical trace from the chamber's temperature recorder. Transition time from the high to the low temperature was noted to be near 45 min. and transition time from the low to the high temperature was noted to be near 15 min.

The assemblies remained in the chamber for 225 cycles at which point they were removed for an initial inspection. Weights were taken on each of these and are recorded in Table 1. Inspection of this data revealed little if any measurable weight loss of each during this period. The assemblies were then given a phenolphthalein leak test that consisted of spraying each thoroughly with an alcoholic solution of phenolphthalein (Ref. 2). This test revealed no signs of leaks on any of the seals but an indication of minute leaks in a few of the fittings. These fittings were subsequently tightened and found to be leak-free thereafter. Next the assemblies were each subjected to another helium leak test as above. To avoid possible damage to the detector the assemblies were first drained of their electrolyte, and then cleaned and dried before carrying out the helium test. Results again revealed that each of these again exhibited leak rates less than $1.8 \times 10^{-9}$ atm-cm$^3$-He/s. At this point the assemblies were again filled with electrolyte, sealed off with cap fittings and then reweighed (Table 1). They were then returned to the environmental chamber for additional thermal cycling.

The assemblies remained in the chamber continuously from cycle Nos. 226 through 3804 except for brief periods when they were removed for additional phenolphthalein leak tests as above. These tests were conducted at cycle Nos. 928, 1776, 3468, and 3804. Results indicated no signs of leaks whatsoever at any of the seals (and also the fittings) of each assembly.

After cycle No. 3804, the assemblies were also weighed and then given another helium leak test as above. Weight data given in Table 1 again indicated that within experimental error there was essentially little if any weight loss in any of the assemblies. This point was confirmed by the subsequent helium leak test that again revealed leak rates less than $1.8 \times 10^{-9}$
atm-cm$^3$-He/s for each of the assemblies (including seals and fittings). Finally, no visible signs of corrosion or deterioration were found, as shown in Fig. 11. On this basis then the seals were found to successfully withstand at least 3804 of the above thermal cycles (7608 h or over 10 months) with little or no development of leaks. Leaks, if present at all within these seals, occur at rates no greater than and most likely less than $1.8 \times 10^{-9}$ atm-cm$^3$-He/s.

After completion of the above tests the assemblies were refilled with KOH, sealed off with fittings, and continued on thermal cycling. Status of these units will be given at a later date.

IV. DISCUSSION

Heretofore there have been three major kinds of seals that have been used for sealing the terminals of aerospace Ni-Cd cells. These may be classified as the ceramic-to-metal type, the glass-to-metal type, and a combination of the glass- and ceramic-to-metal type (Ref. 13).

Of these three, the one that has been shown to be the most promising for this application is the plain ceramic-to-metal type. This is attributed to the fact that the two above types that employ glass have been shown to be inferior to the ceramic-to-metal type on two accounts. First the glass types are more brittle than the plain ceramic types and are therefore more prone to crack. Secondly the glass-to-metal types have been found to be less chemically stable than the ceramic-to-metal types in the battery environment. This is in turn attributed to the known reactivity of the glass component with concentrated KOH solution. As a consequence, the ceramic-to-metal seals have been used most extensively in flight batteries.

Figure 12 gives details of a typical ceramic-to-metal seal that has been used in these flight batteries. Major components consist of a terminal post surrounded by a cylindrical ceramic insulator that in turn is connected to the cover via a metallic stress-relief member. A cup assembly surrounds the lower portion of the ceramic to prevent leakage in the annular space between the terminal post and ceramic. The terminal post is usually made of stainless-type 304 steel or pure nickel. The case is usually made of stainless-type 304 or 304-L steel. The ceramic is a high-alumina type with
95 to 98% $\text{Al}_2\text{O}_3$. The collar and cup are made of Alloy 42, which is an Fe-Ni alloy with thermal expansion characteristics that match those of the alumina ceramic. The assembly contains four braze joints consisting of two metal-to-metal and two ceramic-to-metal types.

The ceramic-to-metal joints are made by first metallizing the ceramic portion. This was originally carried out by the so-called multimanganese process but this has been replaced by the so-called active metal process employing titanium hydride (Ref. 13). The metallized ceramic is brazed to the metallic member with a silver-copper brazing alloy. The metal-to-metal joints are either brazed with the same alloy or tungsten gas welded.

Although a large number of these ceramic-to-metal seals have been used and proven satisfactory in flight batteries to date, there are numerous others that have failed in ground test and would have undoubtedly caused battery failure in space. Reports on sealed Ni-Cd cell tests at Naval Ammunition Depot (NAD) Crane and elsewhere reveal that a small percentage of these seals develop leaks within their first year of life and a much larger percentage develop leaks from their first to fifth year of life (Refs. 6, 12, 13, and 14). On this basis, then, the ceramic-to-metal seals can hardly be considered the optimum for all aerospace batteries especially those that are intended for long term (5 to 10 year) missions.

The major problems that cause leaks with this type of seal are (Refs. 13, 14, and 15):

1. The silver component of the braze has been found to corrode and migrate from the positive to the negative terminal; in addition, this corrosion can cause an internal short circuit.

2. The Fe-Ni alloy members are subject to corrosion because of a couple between these members and the stainless steel cases or because of the presence of small amounts of acid fluxes that are used in brazing.

3. Thickness of the brazed areas has been noted to be quite uneven in some seals with certain areas that exhibit very thick sections and other areas that exhibit dangerously thin sections. This problem has been traced to the jiggling operation that is extremely critical for this type of seal.
Metal has been found on occasion to have penetrated into the ceramic. This is attributed to excessive temperature and/or time for the brazing operation.

The ceramic has been found on occasion to have been fractured and also to have separated from the braze. This is attributed to excessive cooling rates after the brazing operation.

The injection molded Ziegler seal is not, however, subject to any of the above problem areas. First this seal contains no braze materials that are subject to corrosion that causes the shorting problem. Next the seals do not require the use of the stress-relief members that are also subject to corrosion. All components of the injection molded seal including barrel, bushing, and terminal rod are made of materials that are much more inert than those that are employed in the ceramic-to-metal seal. In addition, the injection molded seals can be made without adhering to rigid tolerances for machining and alignment of parts. Finally, the injection molded seals are made without any heating operations that contribute to many of the above problems.

Based on the limited results obtained to date, it is not possible to rigorously show that the injection molded seals are superior to the ceramic-to-metal seals in terms of reliability and life. Similarly, it is not possible to show that these seals will meet the requirements of long term (5 to 10 year) space missions. To establish these points it will be necessary to fabricate and test large numbers of these seals for long periods of time and in actual rather than simulated cells. Plans are underway to carry out such tests.

Results to date do, however, suggest that the injection molded seal is at least a possible alternate to the ceramic-to-metal seal and may offer more reliability than the ceramic-to-metal seal for the long term missions. The basis for these opinions is not only the lack of problem areas associated with the injection molded seal, above, but also the results of the thermal cycle test described in Section III. Therein it was noted that all 5 out of 5 seals successfully withstood 10 months of these severe environmental conditions without developing any leaks greater than $1.8 \times 10^{-9} \text{ atm-cm}^3\text{-He/s}$. Based on the known failure rates of ceramic-to-metal seals under less severe conditions and the discussions of McHenry (Ref. 6), it is quite unlikely that the ceramic-to-metal seals would have demonstrated such excellent
performance as the injection molded seals under the same test conditions. Plans are currently underway to establish this point by carrying out comparable tests to the above with existing ceramic-to-metal seals.

Results to date also establish other significant points. First it has been shown that there are no major problems involved in scaling up the BTL small-size (5 A) version of these seals to the larger size (up to 50 A) version suitable for most JPL flight batteries. Performance of these larger seals has been found to be comparable to that of the smaller seals in that the former have successfully completed over 3800 thermal cycles to date while the latter have successfully completed over 3400 such cycles. Next it has been shown that there is a minor problem of voids in the bushing material and that closer controls should therefore be placed on the injection molding process. It is also interesting to note that the nylon 6-6 bushing performed its function well for the indicated 10-month test period. Therefore this material apparently degrades at a lower rate than first anticipated and it need not be ruled out, at least at this stage, as a candidate bushing material for long-life seals.

Finally, it is interesting to note that the performance of the ceramic-to-metal seals compares very favorably with that of gasket-type compression seals employed on commercial cells. The former were noted to withstand at least 3800 thermal cycles while the latter are reported to rarely exceed 200 such cycles.

At this point it is well to mention that other aerospace organizations are seriously concerned with and are attempting to solve the problems associated with the existing ceramic-to-metal seal. Hughes Aircraft Co., for example, is developing an improved ceramic-to-metal seal under an Air Force program for the Low Earth Orbit Battery Program (Ref. 15). Their approach has been to use new inert braze materials, a very high purity ceramic body, and a new "butt seal" geometry as shown in Fig. 13. The new braze materials include pure gold, as well as gold-nickel, gold-copper, and gold-palladium alloys. The ceramic body is more than 99.5% Al₂O₃ with less than 0.05% SiO₂ (which is soluble in the KOH electrolyte). Anticipated advantages of the new geometry over that of the existing ceramic-to-metal seal are (1) greater tolerance permitted in the jigging operation, (2) greater tensile strength of the ceramic-to-metal-braze joints and (3) the metal attachments between ceramic and case do not need to be made of the special alloys that are employed in conventional ceramic-to-metal seals.
General Electric has also developed an improved ceramic-to-metal seal that is quite similar to the Hughes seal in both design and operation (Ref. 16).

The work on these seals was initiated a relatively short time ago so that there has been insufficient time to give them a thorough evaluation, including life testing. Therefore it is not yet possible to compare the performance of these new seals with the conventional ceramic-to-metal seals or the injection molded Ziegler seals described herein.

V. FUTURE WORK

Near term efforts will consist of the following:

(1) Life testing will be continued on the five remaining Ziegler seals as installed on the simulated alkaline cells.

(2) Life testing will be initiated on conventional ceramic-to-metal seals as installed on existing Ni-Cd cells.

(3) A study will be made on the suitability of alternate plastics as material of construction for the bushing. The primary objective will be to ascertain the feasibility of injection molding materials such as polypropylene, teflon, and Kel-F.

Long term efforts will consist of the following:

(1) A large number of sealed Ni-Cd cells will be fabricated. A portion of these will contain the conventional ceramic-to-metal seals and another portion will contain the optimum Ziegler compression seals as determined above. If available, a number of these will be assembled with some of the improved ceramic-to-metal seals described in Section IV.

(2) Several cells of each type will then be placed on accelerated thermal cycle test as above.

(3) The remaining cells of each type will be carried through a typical test procedure employed for flight batteries. This will include acceptance testing, type approval testing, and simulated mission testing.
REFERENCES


REFERENCES (contd)


Table 1. Weight history of simulated alkaline cells during thermal cycling

<table>
<thead>
<tr>
<th>Thermal cycle No.</th>
<th>Notes</th>
<th>Weights of assemblies, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1^a</td>
</tr>
<tr>
<td>0</td>
<td>Initial empty weight</td>
<td>125.3</td>
</tr>
<tr>
<td>0</td>
<td>Initial weight with approximately 70 cm³ of 30% KOH</td>
<td>125.3</td>
</tr>
<tr>
<td>225</td>
<td>Removed for weight and phenolphthalein test</td>
<td>125.3</td>
</tr>
<tr>
<td>225</td>
<td>Drained electrolyte for helium test</td>
<td>-</td>
</tr>
<tr>
<td>225</td>
<td>Refilled with approximately 70 cm³ of 30% KOH</td>
<td>125.3</td>
</tr>
<tr>
<td>3804</td>
<td>Removed for weight and phenolphthalein test</td>
<td>125.3</td>
</tr>
</tbody>
</table>

^a Assembly No. 1 did not contain KOH or gauges.

^b Assembly Nos. 2 and 3 contained pressure gauges.

^c Assembly Nos. 4 and 5 did not contain pressure gauges.
Fig. 1. Standard Ziegler seal

Fig. 2. Crimp-type Ziegler seal
Fig. 3. Diagram of JPL injection molded seal assembly

Fig. 4. Details of JPL barrel-disc assembly

JPL Technical Memorandum 33-588
Fig. 5. JPL compression tool

Fig. 6. Sectioned sample of JPL seal
Fig. 7. Installation of seal in simulated alkaline cell

Fig. 8. Photograph of simulated cell assembly
Fig. 9. X-ray photograph of seal
Fig. 10. Typical temperature chart from thermal cycle test
Fig. 11. Closeup photograph of seal after 10 months of thermal cycling
Fig. 12. Ceramic-to-metal terminal seal

Fig. 13. Butt seal geometry
A program was initiated to develop improved types of terminal seals for aerospace Ni-Cd batteries. The approach used has not involved attempts, such as employed elsewhere, to improve the ceramic-to-metal seal that is now extensively employed for this application. Rather the approach has been directed toward the development and evaluation of new types of seals. Of prime interest in this initial investigation has been the "Ziegler" type of compression seal and in particular the injection molded version developed by the Bell Telephone Laboratories (BTL). A number of these units were designed, fabricated, and evaluated on an accelerated life test under a simulated battery environment. Results have shown that there are no major problems involved in scaling up the BTL small-size (5-amp) seal to a larger-size (up to 50-amp) seal suitable for most JPL flight batteries. Five out of five such seals successfully completed over 10 months of continuous thermal cycling (2-h cycle from -40°C to +71°C without developing any leaks greater than 1.8 x 10⁻⁹ atm-cm²-He/s.)
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