Lead-Acid Battery:

Post Seals for the New Bell System Battery

By L. H. SHARPE, J. R. SHROFF and F. J. VACCARO

A novel post seal has been designed and fabricated for the new Bell System battery. The seal consists of a cylindrical "clamp" of a rigid cured epoxy resin molded in place on the lead posts and a flexible one-piece butyl rubber structure attached to the epoxy and to the battery jar cover. Accelerated tests show that the seal effectively slows lead corrosion. A useful seal life in excess of 40 years is predicted.

I. INTRODUCTION

The posts on all lead-acid batteries are sealed to prevent the escape of sulfuric acid electrolyte from the battery container. If this highly corrosive aqueous solution of sulfuric acid escaped, it would constitute a hazard and a nuisance in a central office. Electrolyte leaking from the seal of a post can create a high conductivity path to ground. This path, connected to the battery, can lead to heating and arcing which may result in the ignition and burning of adjacent combustible materials. In addition, batteries with leaking post seals require costly periodic maintenance. Leaked electrolyte must be cleaned up, neutralized and replaced.

The post seals of many batteries in float operation leak after being in service for times which are incompatible with Bell System objectives of reliable component performance for twenty to forty years. In this paper, we describe a post sealing system which is developed to be compatible with the expected long-lived behavior of the other components of the new Bell System battery.

Post seals (there are three types) on batteries currently in telephone plant have at least two features in common:

(i) They exert circumferential pressure on the post to make the seal.

(ii) They have seal lengths of less than one-half inch. One type of seal is flexible so as to accommodate motion of the post, relative to

the cover, due to plate growth in service. The other types are rigid. None of them offers any redundancy in sealing.

Figure 1 pictures each of the three types of post seals currently in use. Each seal has a relatively short length and acid eventually works its way to external electrical connections or to ground. Two of these designs (Types 1 and 2) are rigid sealing systems so that premature
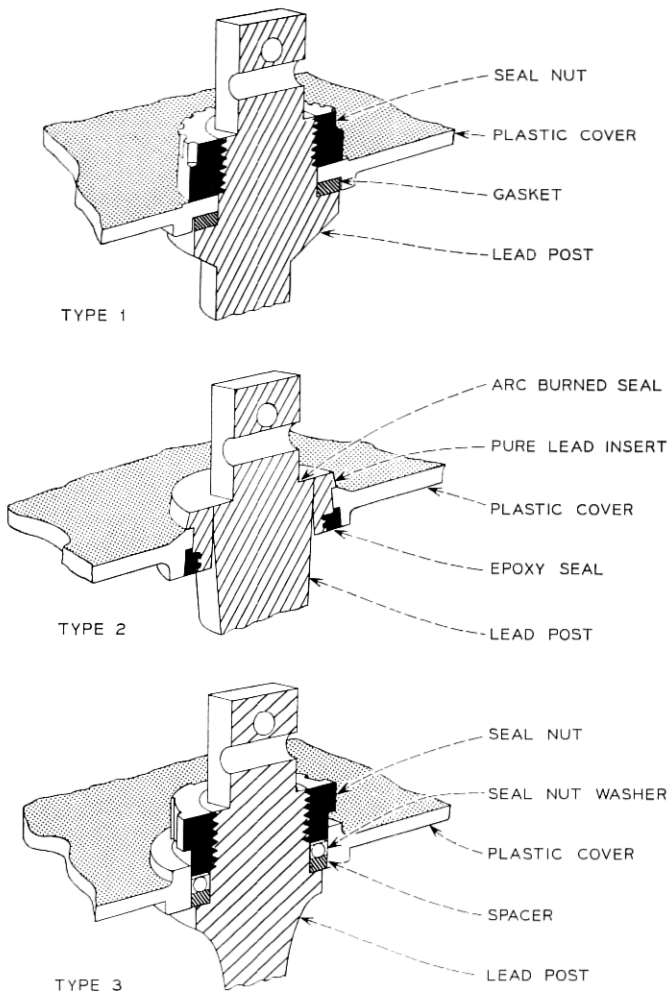

Fig. 1—Current post seals.

failure can occur when element movement (from whatever cause) exerts abnormal stress on the seal.

Because of the hazards involved when post seals leak acid the Bell System defines procedures for maintaining batteries so as to produce a clean and essentially acid-free environment. Proper maintenance requires that the individual cell posts and cover be wiped regularly.

On the basis of the current acquisition rate of 100,000 cells/year in KS 15544/L 400 and 500 series and an average life of 13 years, the total cell population should reach 1.3 million over the next few years. At a very conservative estimate of $6/cell/year for labor costs required to clean cells due to post leakage, this generates a total of $7.8 million in costs per year for the Bell System.

The performance criteria for the new battery post-seals are as follows:

(*i*) The seals must be resistant to acid leakage. Acid may be splashed into the space above the elements during transportation or placement; it will be sprayed above its normal level during gassing; it will attempt, by corrosion and capillarity, to move up the lead posts.

(*ii*) The seals must be compatible with the electrolyte and also with the electrochemical conditions at the posts and the electrochemistry of the battery. That is, the seals and the materials comprising the seals must not be chemically degraded either by the electrolyte or by the corrosive conditions at the posts. Additionally, they must not produce material, in time, at either post, which will alter the electrochemistry of the battery,

(*iii*) They must accommodate motion of the plate stack due to vibration in shipment and plate growth in service. The design objective was that a one-inch vertical motion of the plate stacks and posts relative to the cover be permitted, without breaking the seal.

(*iv*) The seals must be readily manufacturable. Further, procedures for their assembly must be compatible with other assembly procedures for the battery.

II. DESIGN AND CONSTRUCTION

Figure 2 shows early post seals, in batteries currently on field trial, which consist basically of three separate parts.

A *primary post seal* of heat-shrinkable, crosslinked polyethylene tubing which is shrunk to fit tightly on the lead post coated with NO-OX-ID-"A", a nonsoap, thickened, paraffinic grease highly resistant to oxidation.
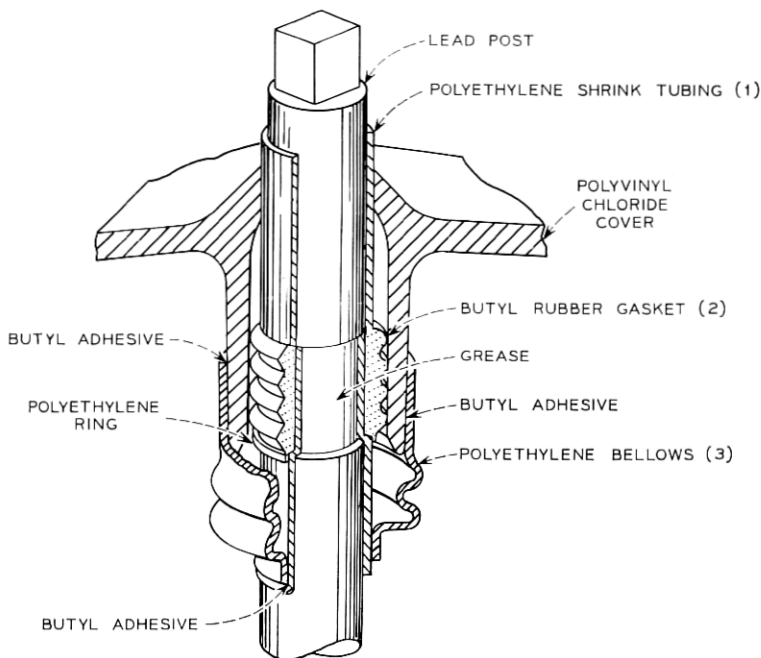
Fig. 2—Three-piece post seal assembly.

A flexible bellows of the same or similar polyethylene (which permits relative motion of the post and cover) joined to the shrink tube and to the skirt of the post hole in the cover with a thermoplastic polyisobutylene adhesive.

A secondary seal which is a corrugated butyl gasket, tightly fitted around the shrink tube, which positions the post centrally in the cover hole and prevents acid and gases from escaping if the bellows should fail. The gasket fits tightly against the wall of the hole but is able to slide against it to accommodate post motion.

These seals were thought to have at least three advantages over seals in batteries presently in service:

(*i*) Corrosion paths to the outside world are longer—an order of magnitude longer than current designs.

(*ii*) They accommodate post motion due to plate growth and element movement during shipment and installation or during an earthquake or nuclear attack.

(*iii*) They provide a redundant electrolyte and gas sealing system.

This three-piece seal, however, has been superseded by other designs mainly because of materials problems and the difficulty of assembling it.

The next logical step in the seal design was the creation of a one-piece seal which combined all of the components of the previous design into a single molded part. This design, which was molded in butyl rubber, is shown in Fig. 3. In it we have the elements of the earlier design—the sleeve, the gasket and flexible bag which performs the function of the bellows of the previous design.

The sleeve is made so as to fit tightly on the post and the seal is assembled as follows. Using the lead post as a plug at the lower end of the sleeve, air pressure is applied at the upper end so that the sleeve inflates slightly. The sleeve is then easily slid over the post, previously coated with either a nonoxidizing grease or a noncuring butyl sealant, into proper position and the air pressure released. The bag is then turned inside out and fastened to the skirt of the cover hole with a butyl adhesive, completing the seal. This one-piece seal takes considerably less time, effort and technique to assemble than the three-piece design.
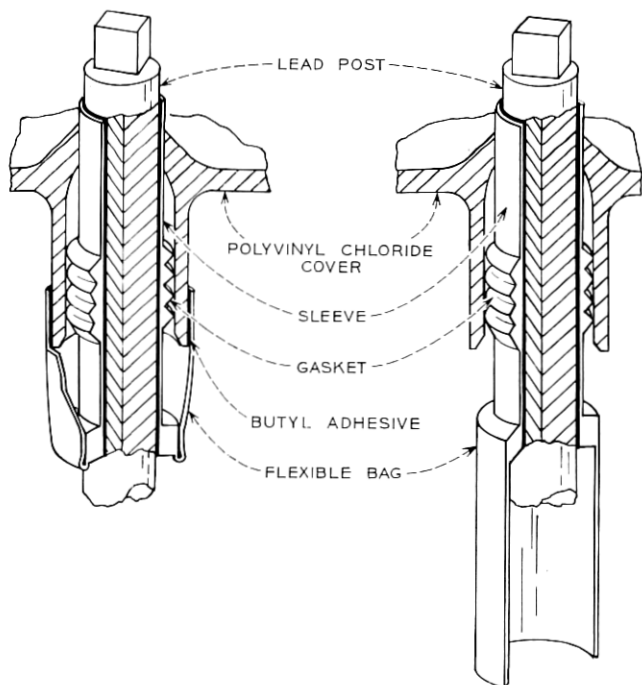

Fig. 3—One-piece post seal assembly.

With respect to the primary post seal, circumferential pressure of the rubber sleeve in combination with the nonoxidizing grease provides a lower limit of corrosion restraint. A multiplicity of clamping rings spaced up the length of the sleeve would provide an additional level of restraint.

A lead-acid cell positive post at a potential above its thermodynamically reversible value will corrode or oxidize. The electrochemical reactions of importance at this post are as follows:

$$2H_2O \rightleftarrows O_2 + 4H^+ + 4e^- \tag{1}$$

$$Pb + 2H_2O \rightleftarrows PbO_2 + 4H^+ + 4e^-. \tag{2}$$
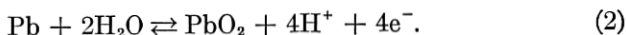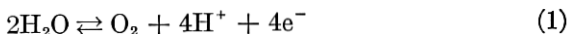
At the positive post, oxygen is evolved at a kinetically controlled rate (equation 1) and lead post material is oxidized (equation 2).

From the above, it is apparent that with corrosion at the positive post there occurs a decrease in density of surface layer material resulting in a volume increase and a larger post diameter. In addition, there is the evolution of oxygen. The volume increase and the evolving oxygen can readily displace a soft or deformable material from the surface of the post and allow electrolyte and resulting corrosion product to progress upward.

When the lead oxide on the negative post is at a polarized potential, it can be reduced and hydrogen liberated. The pertinent electrochemical reactions are as follows:

$$2H^+ + 2e^- \rightleftarrows H_2$$

$$PbO + 2H^+ + 2e^- \rightarrow Pb + H_2O.$$
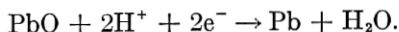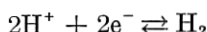
The production of a porous surface with evolving hydrogen could result in rapid capillary flow of acid up the post.

Consideration of the above failure modes dictates the selection of a sealant material which will not readily yield to the stresses developed during lead oxidation-reduction. A restraining cylinder having appropriate mechanical properties and surrounding the post would presumably cause the lead dioxide corrosion product to be produced in the form of a dense barrier offering relatively few capillaries and decreased opportunity for "wicking" of acid up the post. The corrosion rate up the post would then depend upon the compression which the restraining cylinder could provide. The use of a restraining cylinder on the negative post, it is felt, would not result in the generation of high compressive forces in the absence of a volume increase at the surface.

Although there are many mechanical clamping devices available to form a compression seal, material selection and clamp configuration

do present problems. A restraining cylinder of material molded in place on the lead post seemed to offer a relatively simple compression seal in which the complete post length could be utilized. Epoxy resins, cured in place, were selected for the restraining material because they offered favorable chemical and mechanical properties and ease of use.

Figure 4 shows a post seal combining all features of the previous seals with a full length circumferential "clamp" which may be made even more effective by the inclusion of grooves in the lead post. It consists of:

(*i*) The primary post seal—a fairly rigid crosslinked epoxy resin cast around the post-providing a long path length against acid creepage.
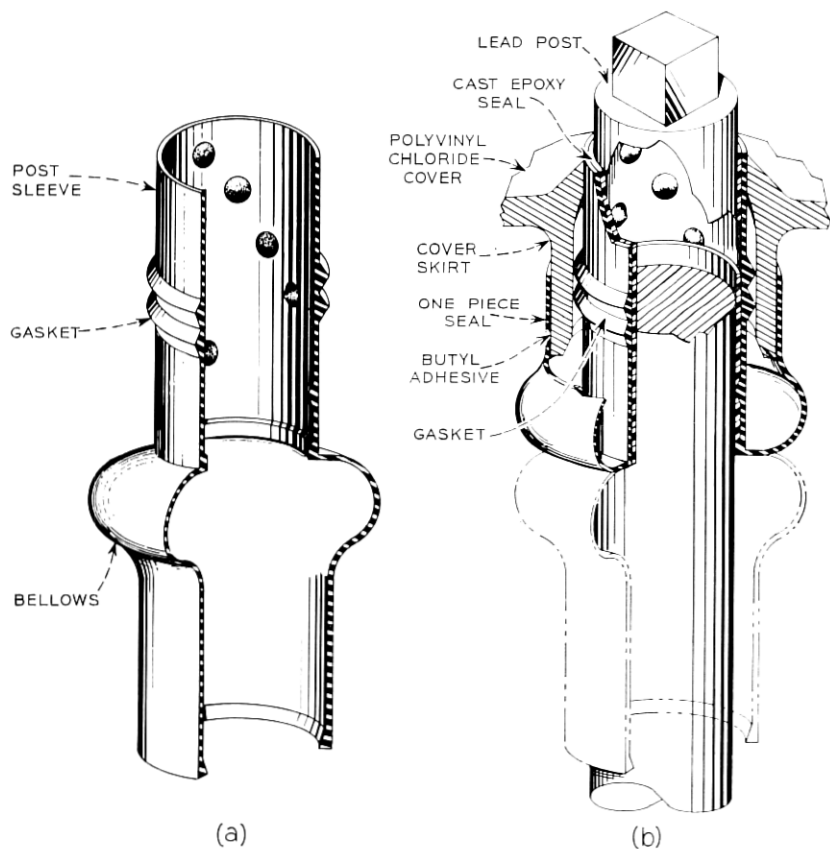

Fig. 4—Final post seal assembly: (a) one-piece post seal, (b) post seal assembly.

(*ii*) The one-piece butyl rubber structure previously described, fitted over the epoxy resin, which provides both the primary and secondary electrolyte and gas seals, that is, the flexible bag and the corrugated gasket.

The sleeve of the one-piece rubber structure has, however, been modified so as to make it serve the function of a mold during casting of the epoxy resin around the post.

Fifteen randomly distributed conical projections are provided on the inner surface of the sleeve. These projections allow proper location of the sleeve on the post providing necessary annular space for molding the epoxy "clamp." The projections also facilitate random flow of the epoxy into the space and flow of air bubbles out. A heavy molded ring at the lower end of the sleeve fits tightly to the post eliminating possibility of epoxy leakage before cure. The curing in place of the epoxy in contact with the sleeve also provides a good joint between the epoxy and the rubber sleeve. The post seal is assembled as follows:

The rubber sleeve is located in place over the post by the conical projections. A supporting fixture is used to enclose the sleeve and prevent bulging during epoxy injection. The epoxy is then injected in the annular cylindrical space between the post and sleeve and cured. The cover is located in the proper position over the corrugated gasket. The bag is then turned inside out and fastened to the skirt of the cover hole with a butyl adhesive, completing the seal.

Materials selection as to compatibility with lead-acid cell performance was of primary concern. After consideration of mechanical properties and design criteria, it had to be insured that the proposed material was unaffected by the acid electrolyte.

The epoxy sealant was evaluated for inertness by performing leaching experiments in 1.210 specific gravity sulfuric acid. The epoxy was first cured in the form of sheets 0.1 inch thick. Pieces cut from these sheets were added to a quantity of acid, maintained at a temperature of $70° \pm 2°C$, such that the ratio of epoxy surface area to solution volume was at least equivalent to that expected in a cell. At predetermined intervals, samples of the solution were removed and cooled to room temperature. After cooling, the solutions were analyzed, by means of the current-potential behavior observed at rotating lead disks under linear potential scan conditions, to determine if electrochemically active materials were present. Scans on the lead disk were both anodic and cathodic in direction to simulate reactions at the negative and positive cell plates. Leaching was continued and scans were made until

the epoxy had become brown in color, indicating severe oxidation. At no period in the acid leach test did the lead disk analysis indicate the presence of materials which would alter the normal operation of a lead-acid cell.

Before acceptance of the butyl rubber for the one-piece seal material, it was also examined by a method similar to the above. Leach solution was tested by rotating lead disk techniques as well as by additions of butyl rubber-acid solutions to charged cells with pasted plates. This material also proved to be clean electrochemically. Materials selection and the details of assembly procedures and techniques are not yet final. However, we expect that the general features of both post seals in the final design of the new Bell System battery will be as we have just described them.

III. ACCELERATED TESTING AND RESULTS

Accelerated degradation of the primary post seal for test purposes was accomplished by potentiostating the lead post with proposed seal at a relative high overpotential in standard battery electrolyte. The increase in corrosion rate at the current densities required to maintain the test overpotentials results in accelerated progress of electrolyte and resulting corrosion product up the lead post. Tests were carried out at normal room temperature ($\approx 75°F$). We did not test at an elevated temperature because we felt that development of thermally induced stresses, heat degradation of materials, and so on, would unnecessarily complicate analysis of seal behavior.

The primary concern of this study was evaluation of seals for the positive post. The corrosion mechanism, stress and environmental conditions at this post, it was felt, require a seal which should more than satisfy the requirements for a seal at the negative post. Preliminary accelerated test data on negative posts appear to justify the above belief.

Primary post seals were prepared for testing by first abrading lead posts 1.72 inch in diameter to brightness with #600 abrasive paper and then wiping carefully with clean rags. The cleaning technique used was chosen to insure minimum lead surface contamination and oxide formation so as to provide a reasonably well-defined surface on which to begin testing.

The epoxy resin plus curing agent was poured into a removable mold surrounding each post and cured to form a collar 0.1 inch thick and several inches long. Coatings less than 0.05 inch thick severely deformed

and disintegrated during test. The posts were then immersed in sulfuric acid (1.210 specific gravity) with the bottom of the epoxy collar submerged in the acid about 1 inch. Several posts were potentiostated at each of three voltages, that is, +1.16 V, +1.30 V, and +1.50 V relative to a $Hg/Hg_2SO_4/H_2SO_4$ (1.210 specific gravity) reference electrode. The voltage +1.16 V is the positive post potential of a battery under normal float conditions. The other potentials represent accelerated test conditions. Since the epoxy coating is transparent and the corrosion product dark brown, it was possible to observe and measure visually the progress of corrosion up each post. The precision of this measurement was better than ±0.010 inch. Measurements were made at 60-day intervals to determine a corrosion rate at each voltage.

Initial concern in any accelerated test procedure is that the accelerating parameter influence only the rate at which reactions take place. Alternately stated, accelerated testing should not cause reactions to occur which would not ordinarily occur at unaccelerated conditions. Temperature as an accelerant, for example, was rejected since it was felt that the reaction mechanism might change at elevated temperatures.

Voltage, more precisely current density, was selected as the accelerating parameter. It was then necessary to ascertain that the increased voltage influenced only the reaction rate of corrosion at the positive post. This was accomplished by potentiostating lead posts at each of the three above mentioned positive potentials.

At 60 days, voltage was plotted against corrosion rate on linear coordinate paper (see Fig. 5). The resulting linear relationship for this relative short period indicates the consistency of the reaction mechanism at the various voltages. Calculation of an acceleration factor from these data yields one day at 1.50 V as being equivalent to approximately nine days at 1.16 V (float potential). Plotting data at the 60th day, it was felt, would reflect purely corrosion phenomena with minimum influence due to resultant compressive forces or height of corrosion on the posts. Data at an early time for the 1.16 V test condition, however, would also include substantial measuring uncertainties.

Figure 6 graphically portrays the progress of corrosion up the positive post with time. Two potentials are plotted, +1.50 and +1.16 V, representing the accelerated and float conditions respectively. It is significant that the slope of the curve for 1.50 V is markedly decreasing with time. This decrease in slope or corrosion rate can perhaps be attributed to the production of compact corrosion product as previously hypothesized. Similar data for 1.16 V would require a number of years to obtain, although the current corrosion rate is approximately 0.2 inch/year.
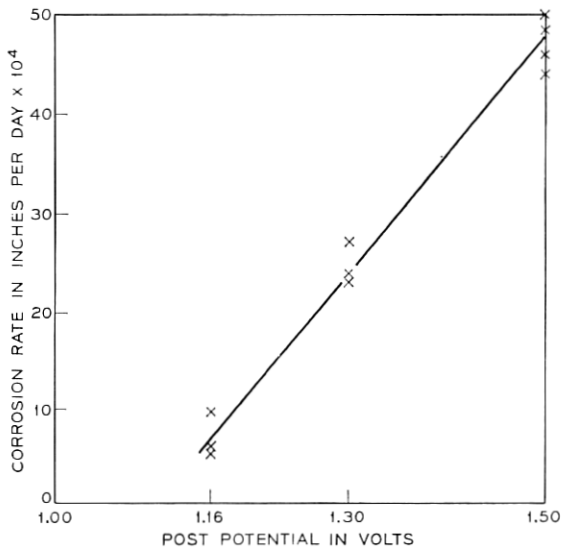
Fig. 5—Corrosion rate as a function of positive post potential.
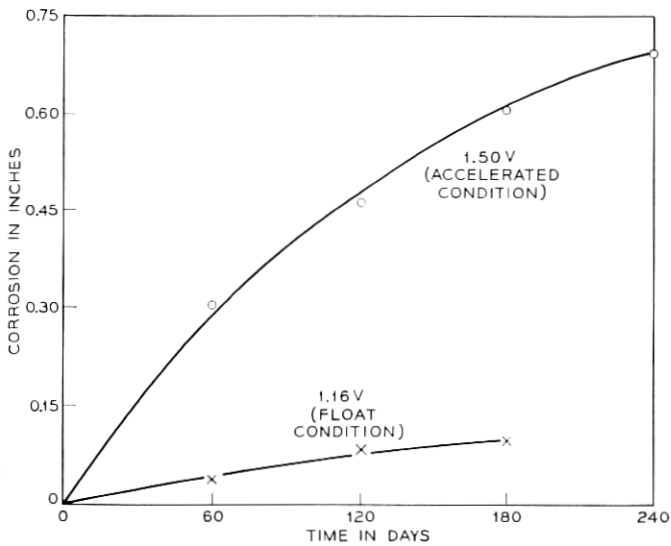

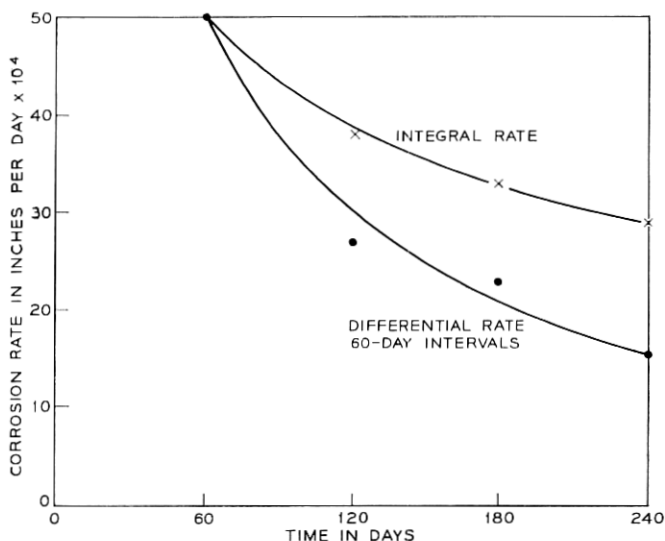Fig. 6—Corrosion of positive post as a function of time.

Fig. 7—Corrosion rate of positive post as a function of time (1.50 V).

The decrease in corrosion rate with time is plotted on an integral and differential basis in Fig. 7. It is apparent that the corrosion rate has decreased to 30 percent of its original value from the first (60th day) to the fourth (240th day) 60-day interval. These incremental slope changes contribute to the 40 percent decrease in the integral corrosion rate plot. From the data for the 1.50 V test, it is apparent that the presently observed corrosion rate (0.2 inch/year) at 1.16 V can realistically be expected to decrease to one-half or 0.1 inch/year, which would yield a useful seal life of at least 40 years.

IV. CONCLUSIONS

A novel post-seal has been designed and fabricated for the new Bell System battery. Accelerated tests have been carried out which indicate a useful life for this seal in excess of 40 years. Such a seal life is obtained by:

(*i*) Utilizing long posts, thus providing long path lengths for corrosion,

(*ii*) Stifling corrosion effectively by surrounding the posts with a rigid cast epoxy cylinder,

(*iii*) Permitting relative motion of plate stacks and battery jar cover to accommodate stack motion in service, and

(*iv*) Building redundancy into the seal.

V. ACKNOWLEDGMENTS