REPORT NO. 1223-69

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DEVELOPMENT OF A 300 Ah RESERVE SILVER ZINC CELL FOR AUTOMATICALLY ACTIVATED BATTERY

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1.0 INTRODUCTION

The purpose of this work is to design and develop an automatically activated, single cell- silver-zinc battery, with a nominal capacity of approximately 300 Ah, for deep space exploration.

The battery shall be capable of operating for one year at a shallow cycling regime consisting of twelve hour orbits (one hour discharge followed by eleven hours of recharge) at 33% (100 Ah) depth of discharge. Operating temperature ranges from 0°C to 40°C. In accordance with the terms of the contract, two types of cells will be developed: (1) a dry charged (silver oxide-zinc) unit and (2) an unformed (silver-zinc oxide) unit.

The scope of the work includes:

(a) cell design,

(b) construction and testing of cell prototypes (in reduced scale for determination of gas evolution rates and in full scale for electrical testing),

(c) design of an activation system,

(d) design of battery layout,

(e) construction and testing of 2 finalized batteries and

(f) construction of deliverable items.

During the period covered by this report, the following has been accomplished:

(a) A preliminary design, for both dry charged and unformed cells has been made.

(b) Six cells of the above design (3 of each type) have been built and testing started.

(c) Eight cells of similar design, but scaled down to approximately 5 Ah size were also built. Six of these cells were provided with pressure gauges and gas evacuation fittings. Initial tests results on these cells are also available.

(d) An activation system has been devised and will be ready for testing shortly.

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2.0 STATEMENT OF WORK

2.1 Cell Design

The design effort in this program was devoted to incorporating the latest state of the art technology into the cell, compatible with the performance requirements specified in the contract and summarized in the introduction to this report.

2.1.1 Positive Electrodes

As mentioned in our Technical Proposal of April 1969, work done on Contract NAS 5-345 showed an improvement in silver utilization by decreasing the powder density. The best results were obtained from electrodes at a density of about 4.2 gm/cc. This figure was used for the positive electrodes of both dry charged and unformed cells.

After the construction of the prototype cells had begun, it was decided, as suggested by NASA, to consider the use of positive plates with electrodeposited surface film of calcium hydroxide. The process, developed at Hughes Aircraft on a NASA contract, is believed to slow down considerably the migration of silver through the cellulosic (C-19) separators, thus extending the life of the cells.

The plates would be manufactured by Yardney, the usual way, and sent to Hughes for the electrodeposition of the $Ca(OH)_2$. Since the process adds about .003 in to the thickness of each plate, a slight cell redesign would be required. A detailed proposal on the subject is presently being prepared to be submitted to NASA.

2.1.2 Negative Electrodes

Several techniques, aiming at the problem of reducing the shape change of the negative electrodes, the single major factor responsible for the capacity decay of silver-zinc cells, were incorporated in the design of the cells for this program. They include:

(a) Use of Teflon emulsion in the plates.

(b) Addition of nylon fibers.

(c) Use of oversized (extended edge) negatives.

(d) Increase of the zinc to silver ratio.

The Teflon, in combination with the fibers, acts as a binder of the ZnO particles, considerably increasing the mechanical strength of the electrodes. Oversized negatives are aimed at eliminating the high edge current density that results when positive and negative plates are of the same size. The high zinc to silver ratio is most useful in the latter stages of the life of the cell, when a reserve of negative active material is required to compensate for inevitable capacity losses.

Another approach for the improvement of the cycle life capability, the fabrication of specially contoured negative electrodes, was not employed in this program because of the great difficulty involved in the manufacture and quality control of the plates.

2.1.3 Separator System

As mentioned in our Technical Proposal, no separator has been developed that can match the mechanical and electrical properties of cellophane. Therefore, YEC's proprietary silver treated cellophane, C-19, will be used as main separator.

In order to improve the life expectancy of the cell, it was decided to increase the number of turns of C-19 from the originally proposed five turns to six. This should provide at least 1 year of activated cell life.

Five mil Pellon (style 2506-K4, without wetting agent) consisting of 100% polyamide fibers, heat sealed as a bag, was used as a positive inter-separator.

The positive plates were wrapped individually by placing them in the Pellon bags and then each group of two plates was wrapped with six turns of C-19; the assembly so formed was folded into a "U" and the negative plates, unwrapped, except for the aldex paper used for their manufacture, were placed in the center of the "U" and between "U"'s.

Note: In our Technical Proposal it was noted that several methods to eliminate the "U" wrap were being evaluated. These included:

(a) individually wrapped positive plates, with an open bottom wrap, which would be closed with a silver or plastic rail, either crimp sealed or epoxy sealed.

(b) An accordion wrap, with an epoxy sealed bottom.

However, it was decided that both of the above methods are mechanically difficult and of dubious reliability; furthermore, there is no test data available to prove their superiority over the "U" wrap.

Inasmuch as the occurrence of shorts at the bottom fold of the "U"'s have been extremely rare, we still feel that this is the simplest and safest way of wrapping the cell electrodes.

2.1.4 Electrolyte

For this application, the electrolyte used is a 45% KOH solution, with 80 mg/ml of ZnO dissolved in it and purified with zinc dust.

The ZnO is added to minimize the dissolution of zinc from the plates, a reaction that would be accompanied by heavy gassing. The zinc dust entraps iron particles, thus recovering them from the solution. This is very important because the iron, even at very low concentrations normally present in KOH solutions, induces gassing of the cells.

2.1.5 Preliminary Design Summary

Several modifications to the design given in our Technical Proposal were introduced; they include:

(a) increase of number of plates from 10(+)/11(-) to 14(+)/15(-), to lower the current density during the 100A discharges and the subsequent charges.

(b) increase number of layers of C-19 from 5 to 6 (see paragraph 1.3).

(c) change of positive electrode grid from No. 4/0 to No. 1 exmet, since it was felt that a heavy grid was unnecessary for one year operation.

(d) change of case internal and external thickness to provide the additional space required by changes (a) and (b).

(e) change negative electrode grid from No. 1/0 silver exmet to perforated silver foil, to avoid the danger of short circuits caused by exmet spears, when the collector is exposed due to zinc shape change in the latter period of the cell's life.

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Positive Electrodes

Number per cell:	14
Size:	3.50"W x 8.06"h x .034"th.
Active material:	100% silver powder
Mass of silver:	64.3 gm/plate x 14 plates = 900 gm
Silver density:	4.20 gm/cc
Collector:	Silver exmet No. 5Ag15-1
Leads:	One silver tab, 1/8" x .008"

Negative electrodes

Number per cell:	15 (half end negatives)
Size:	3.75"W x 8.31"h x (.079"th [full] (.041"th [half]
Active material:	93% ZnO + 2% HgO + 5% Teflon with .04% nylon fibers
Mass of zinc:	71 gm/full plate = 994 gm/cell.
Mass of zinc excluding oversize:	900 gm/cell
Zinc density:	2.00 gm/cc
Collector:	.0009"thk perf silver foil, 8C Beckley pattern
Leads:	One silver tab, 1/8" x .008"

Separator System

(a) Positive:	Heat sealed bag consisting of one layer of untreated Pellon P-5.
(b) Main:	"U" wrap, consisting of six turns of C-19.

Electrolyte

45% KOH solution, containing 80 mg/ml of ZnO and purified with Zn dust

Case and Cover

The cases and covers of the experimental cells were fabricated of lucite, .125" thick. Sketches of the case and cover are attached to this report (Figs. 1 and 2).

Cell Weight and Dimensions

The dry weight averaged 3017 gm for the unformed cells and 2845 for the dry charged cells. The cells were filled with 740 cc of electrolyte of specific gravity 1.518. The cell external dimensions are: height, 11.10 in. to the top of the case and 11.75 in to the top of the terminals; width, 4.20 in; thickness 2.60 in.

Notes:

(1) The design and construction of the dry charged cells is identical to that of the unformed cells; the only difference is that in the former, the positive and negative electrodes are charged before assembly.

(2) The cell case and cover will have to be slightly modified for attachment of the activation system.

2.2 Performance of 5 Ah Cells

These cells were tested primarily to determine their gassing rate under various conditions. At the time of writing this report, most room temperature tests were completed, including stand immediately after filling, charges and discharges.

In order to simulate the actual conditions under which the cell is to be used, six of the cells (3 unformed and 3 dry charged) were sealed immediately after filling, with pressure gauges and gas evacuation valves attached. The cells were allowed to stand for 96 hours and the pressure was monitored periodically. As expected, some pressure build-up was observed in the dry charged cells, however, the rate of evolution was surprisingly low, and the pressure stabilized at values ranging from 1 to 3 psig.

There was little or no gas evolution in the unformed cells; at the end of 96 hours, their pressure was slightly below atmospheric (-1 to -5 in. of Hg).

At the completion of this test, the cells with gauges were pressurized to 15 psig with nitrogen and allowed to stand for 4 hours to check for possible leakage of the gauges and/or evacuation valves. No traces of leakage were apparent in any of the units.

After restoring to atmospheric pressure, the cells were given several cycles at room temperature,at current densities similar to those anticipated for the full scale cells. During this entire cycling program, none of the cells showed any significant positive pressure; the highest pressure observed was 3.5 psig in a cell, probably due to a slight overcharge.

2.3 Performance of Full Size Prototypes

Six full size prototype cells were built: Nos. 9, 10, 11 (unformed) and 12, 13, 14 (dry charged). The unformed cells were allowed to soak for 72 hrs., and then given two formation cycles, as follows:

Cycle F-1 (Charge: 6.0A to 2.05V
(Discharge: 50A to 1.00V

Cycle F-2 (Charge: 9.0A to 2.05V
(Discharge: 50A to 1.00V

The results were as follows:

	Cell No. 9 Output (Ah)	Cell No. 10 Output (Ah)	Cell No. 11 Output (Ah)	Average Output (Ah)	Plateau Voltage
Cy F-1	355	340	350	348	1.48
Cy F-2	350	317	334	334	1.49

The dry charged cells were allowed to soak for 72 hrs. and discharged at 50A to 1.00V, with the following results:

Cell No. 12 Output (Ah)	Cell No. 13 Output (Ah)	Cell No. 14 Output (Ah)	Average Output (Ah)	Plateau Voltage
383	374	380	379	1.45

At the conclusion of the above cycling, all cells were sealed and placed in a shallow cycling regime similar to that foreseen for actual use:

Charges: 9.0A to 2.00V (approx. 11 hrs)
Discharges: 100A for 1 hr.

Every 10 cycles, the cells will be drained at 50A to 1.00V to check their capacity.

2.4 Activation System

The design of an activation system for the battery presents peculiar problems, resulting from the following factors:

(a) The battery is to be activated in a zero gravity, zero pressure environment.

(b) The possibility of releasing by products of the activation process to the interior of the space vehicle where the battery operates or to space is precluded (except perhaps under carefully controlled conditions) due to the risk of damaging equipment on board, clouding lenses of optical instruments or even altering the course of the probe.

(c) Fast activation is not required; in fact it would be disadvantageous because the slow absorption of KOH by the cell separators would result in accumulation of large quantities of liquid outside the cell pack and/or excessive pressure build-up.

The absence of gravity will presumably cause the electrolyte and the air inside the cell to disperse randomly, instead of the normal configuration of electrolyte at the bottom and air at the top, occurring in cells operating in the upright position and subjected to the earth's gravity.

The effect of this electrolyte-air configuration on cell performance is not known because of total lack of experimental data; based on theoretical considerations, it should be beneficial due to the more uniform distribution of electrolyte throughout the cell pack that may eliminate irrigation problems which are very common in tall cells with heavy separator system. The zero gravity and random orientation of the battery will, of course, eliminate any activation device in any way dependent on the effect of gravity.

The necessity of activating slowly and the ban on gas release to the outside of the battery led to the abandonment of any conventional activation system based on gas generators, which are used in most reserve type batteries.

A system based on a diaphragm and a spring, released by a power squib, has been devised. A preliminary design, subject to modifications, is sketched in figure 3.

The electrolyte before activation is contained in a reversible diaphragm (bellofram) and in the top section of the activation cylinder. A diaphragm or breakoff tube prevents it from entering the cell. The bellofram is made of buna-N rubber, reinforced with dacron; it is unaffected by KOH and designed for up to 1000 cycles which makes it highly reliable for the single application required. The bottom of the bellofram rests against a piston under which there is a spring, held compressed before activation.

The activation is accomplished by activating a power squib (gas free) with a dual function:

(a) Release of the spring

(b) Rupture of the diaphragm or breakoff tube that connects the activation cylinder to the cell.

The electrolyte starts flowing into the cell slowly, since air pressure inside it builds up; however, air is expelled from the cell and into the air sump in the back of the activation cylinder through four Zitex membranes. These porous membranes, consisting of processed Teflon, are discs, approximately 3/4 in. dia., manufactured by Chemplast Inc., Wayne, N.J., which allow the passage of air and other gasses, but are impermeable to liquids. The membrane selected for this application is No. E610-122D, with a rated air flow of .86 sec/100 cc x in^2 at .2 psi pressure differential.

The number and location of these membranes is such that practically insures against the possibility of all of them being flooded with electrolyte (and therefore unavailable for gas transfer). The expulsion of air from the cell is helped not only by the pressure of the electrolyte inrush, but also by the vacuum generated in the air sump by the displacement of the piston.

It should be noted that the above described activation system functions independently of the battery's attitude, and of course, of any gravitational force (or its absence).

Details in the construction of the system and materials for some of its parts have not yet been finalized and will be included in the next report.

Note: This activation system may be complemented by the use of a hydrogen diffusion membrane, as developed by Melpar, Inc. (cf. Melpar's report of March 1966, prepared for NASA G.S.C.F. on contract No. NAS 5-3753). This membrane, consisting of electrodeposited Palladium black on Silver-Palladium rods, may be placed on the cell cover, or preferably on the air sump.

It should be noted that the gassing tests described earlier in this report seem to indicate that the hydrogen diffusion membrane is unnecessary, however, a final decision on the subject is being held in abeyance for the present.

3.0 PERCENTAGE OF COMPLETION

On the basis of the above statement of work and from a careful computation of time and money expenditures, it is estimated that 35% of the work on the project has been completed to date.

4.0 PROJECTION OF WORK SCHEDULED FOR FOLLOWING REPORTING PERIOD AND SCHEDULE FOR REMAINING ACTIVITY

The work scheduled for the period of October to December 1969 includes the following items:

(a) Completion of tests on 5 Ah cells, including charges, discharges and stand at high (40°C) and low (0°C) temperature.

(b) Continuation of testing on the full size prototypes.

(c) Construction and testing of cells with electrodeposited $Ca(OH)_2$ on the positive electrodes (subject to approval of our proposal by NASA).

(d) Finalization of the design of the activation system and testing of at least one full scale cell-activation system assembly. Complete engineering evaluation of the system.

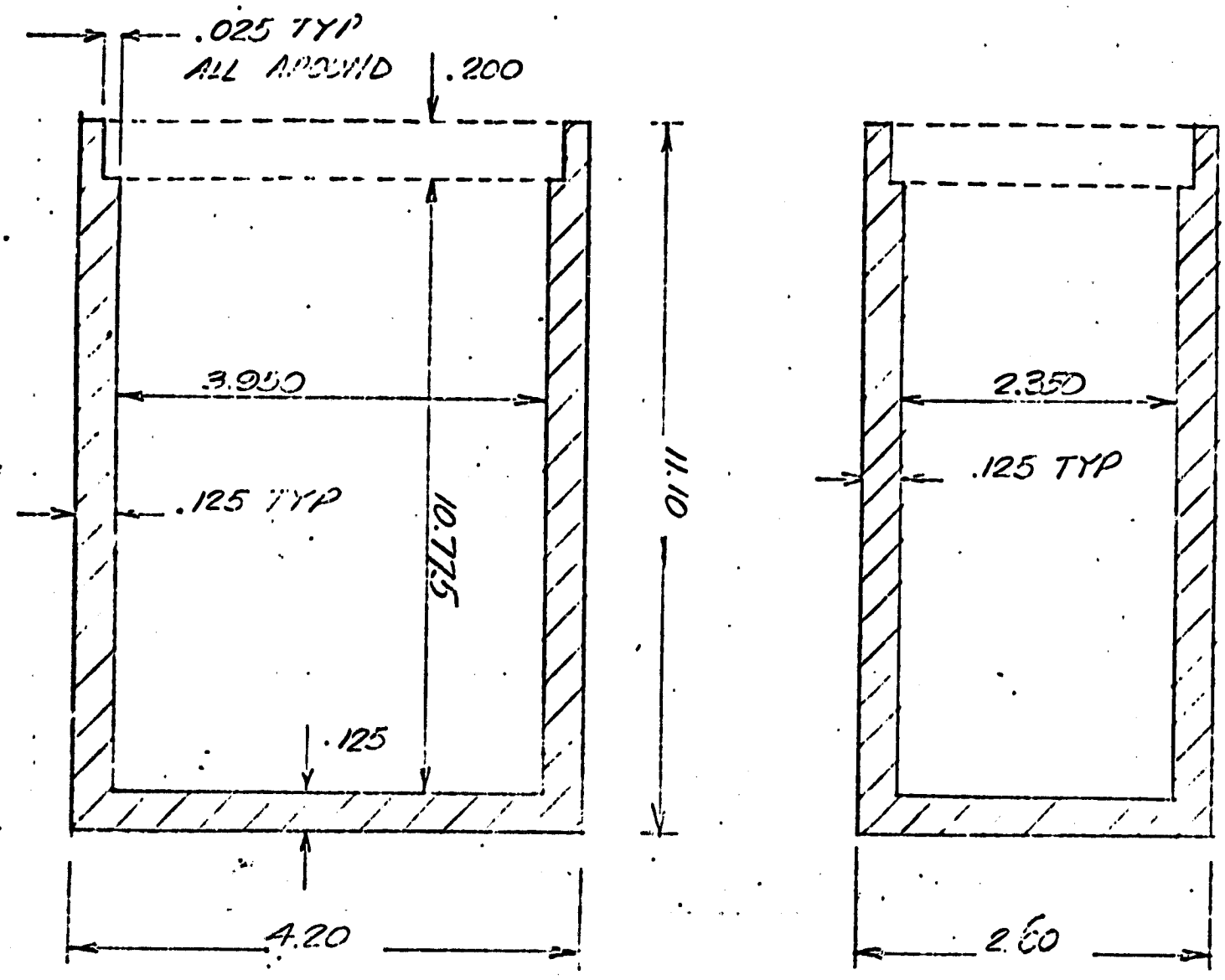
(e) Preliminary battery design and layout.

(f) Design, preparation of drawings and procurement of battery parts, including case, cover, wiring, connecting pins, etc.

The total program time has been increased somewhat by the request to incorporate the calcium hydroxide impregnated plates in the test program (and eventually to the deliverable items), by the fact that program initiation coincided with the summer vacation period; and by the difficulty in devising a suitable activation system. For these reasons, a formal request will be made to extend the period of performance of the contract (see article IV) from 6 to 9 months. The total cost of the contract will not be affected by this delay, except as mentioned in our "Technical Proposal for the Incorporation of Calcium Hydroxide Film ...."

For the above reasons, the remaining activity, which includes (1) completion of testing programs mentioned in items (b) and (c) above; (2) construction and testing of complete battery prototypes and (3) construction of deliverable items, is scheduled for completion by the end of March 1970, with the Final Report, New Technology Report and Materials Report to be submitted within 6 weeks after that date.

LR 300 (5) CELL CASE



NOTES

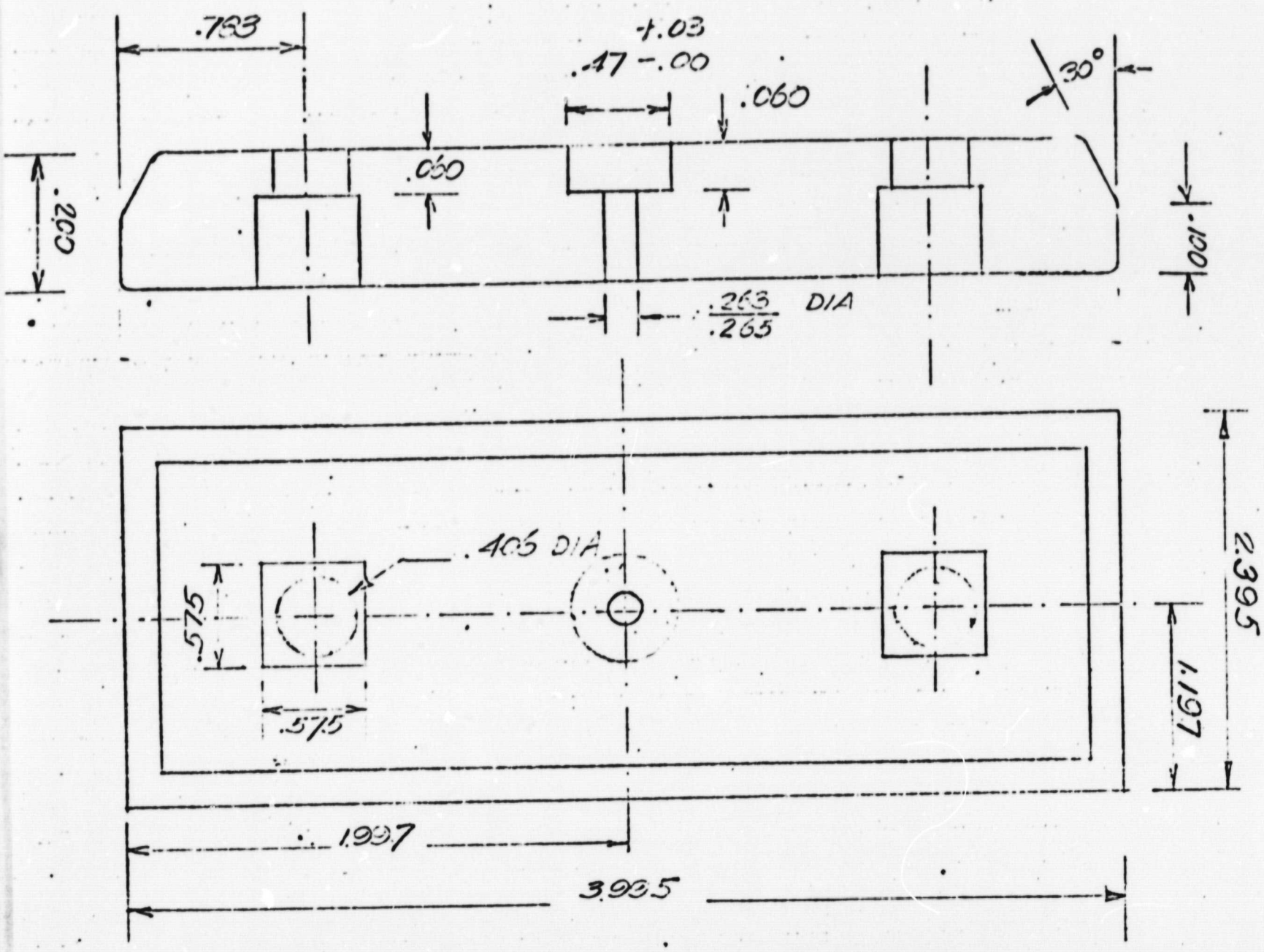
① TOLERANCES : .XX ± .03
.XXX ± .005

② MATERIAL : LUCITE

③ ALL CEMENTED JOINTS TO BE CLEAR AND FREE OF SOLVENT BUBBLES

FIG 1

LC 300(S) CELL COVER



COVER TO FIT CASE WITH .005 MAX CLEARANCE ALL AROUND

NOTES

① TOLERANCES : .XX ± .03
.XXX ± .005

② MATERIAL : LUCITE

FIG 2