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ALKALINE PRIMARY-CELL FAILURE MODE

Douglas Strait NSS 9707

I recently experienced an alkaline cell failure via a mechanism previously unknown to me. The cell experiencing this failure was one of the 4 cells within an Eveready Energizer(™) #529 6V lantern battery. Fortunately, this battery had been tested before use in such a way as to preclude ascribing this failure to previous abuse or gross manufacturing defect. Prior to using alkaline cells or batteries, I routinely test them under load. My standard test for 6V lantern batteries or sets of 4 "D" cells is to apply a load of 0.7A (with the battery at room temperature) and to measure the terminal voltage after 1 minute. I have found this to be an effective means of detecting batteries containing weak or defective cells. The battery containing the cell which later failed was initially tested via this method and determined to be good. The battery was used under normal caving conditions for 7 hours during which performance was satisfactory and approximately 40% of the nominal capacity was removed. The battery was subsequently stored in a refrigerator for 6 months with the exception of 3 or 4 occasions when it was transported in my truck on caving trips but not used. Total estimated distance of truck transportation subsequent to the initial 40% discharge was in the range of 5000-6000 miles. I happened to use this battery to test a light and noted that the terminal voltage under load was markedly lower than expected based upon the discharge history of the battery. Because I was curious about this, I decided to investigate further. I removed the sheet-metal cover from the battery to permit access to the individual cells. I measured the individual cell voltages under load and found 3 to have voltages consistent with the battery discharge history and the fourth cell to have a much lower voltage. None of the cells exhibited leakage or signs of physical abuse. I then disassembled the "bad" cell and one of the "good" cells. The visual appearance of the interior of the two cells was essentially identical with the notable exception that the anode current collector which consists of a piece of brass sheet metal was silvery in appearance in the "good" cell and darkened in the "bad" cell. I knew from previous cell autopsies that the anode current collector normally retains its silvery appearance even in completely discharged cells. I decided it was time to seek professional help. I contacted the Eveready Southeastern Region Engineering Assistance Office and eventually was connected with someone who probably knew the answers to my questions. As a relevant aside, in 20 years of dealing with technical representatives of countless products, I have never encountered an individual who was more actively unhelpful than this person I spoke with. Some of the information presented here are my inferences based upon this conversation. When given the opportunity, the Eveready technical representative declined to confirm or deny most of my inferences. When I described what I had done and what I had found, the first question I was asked was whether the battery had been subjected to shock or vibration. Believing that 5000-6000 miles in the back of my pickup qualified, I responded - YES. The Eveready Tech Rep volunteered that there is a "rare" failure mode associated with shock and vibration consistent with my observations. He declined to characterize the relevant levels of shock/ vibration or the probabilities of failure. The more specific my questions became the less candor his answers contained. I managed to determine that the darkened anode current collector is an indicator of this failure mode. I also concluded that in the case of the Eveready cells (and presumably those of other manufacturers) the effort to reduce or eliminate mercury in these cells has significantly increased the occurrence of this "rare" failure mode.

What action is appropriate given the very limited information we have on this failure mode? I suggest the following:

1. Avoid subjecting your batteries to unnecessary shock and vibration.
2. Where high confidence in battery capacity is required such as when a single battery is to be taken on a long cave trip, test the battery immediately prior to use. As previously described, I test alkaline lantern batteries and sets of 4 "D" cells by measuring the terminal voltage 1 minute after application of a 0.7 amp load. For my uses, approximate remaining capacity is given by the formula $\% \text{capacity} = (V - 3.00) / 3.00$. This formula at best gives a fair approximation of capacity. You will find that new batteries will typically yield a capacity figure of 90-95%. I use an LM317T voltage regulator configured as a constant-current sink for the 0.7 amp load. This test should be performed at 68 to 77°F [20 - 25°C] for best results.

INCANDESCENT LAMP PARAMETER VARIATION WITH VOLTAGE

Douglas Strait NSS 9707

Most readers are probably familiar with the way in which incandescent lamp parameters (current, life, light output, efficiency, etc.) vary in response to applied voltage. Most lamp manufacturers publish this information as a table or graph. These tabular or graphical data are derived from a set of equations that relate the parameter of interest to the applied voltage, via voltage raised to an exponent. These exponents are based upon a composite of various designs of lamps. Typical exponents used are 1.8 for efficiency (efficiency varies as voltage raised to the 1.8 power), 3.5 for light output (light output varies as voltage raised to the 3.5 power), 0.54 for current (current varies as voltage raised to the 0.54 power), and 12 for lamp life (lamp life varies inversely as voltage raised to the 12 power).

I have long been intrigued by a footnote that some manufacturers include with these data. The General Electric Miniature lamp catalog is typical in stating "...these data) are approximate only between 95% and 110% of rated voltage...will not apply to lamps with lives in excess of 5000 hours or to halogen-cycle lamps".

While lamps with design lives in excess of 5000 hours are of little interest to cavers, halogen-cycle lamps as well as operation outside of the 95%-110% of design are relevant. To satisfy my curiosity, I contacted the General Electric incandescent lamp guru. According to him, these formulas are good approximations for voltage variations far beyond the 95%-110% of rated range and also apply to halogen-cycle lamps provided that the lamp envelope temperature remains above the minimum required for the halogen cycle to operate.

I performed an experiment to determine the applicable exponent for variation of lamp life with voltage when operating far above design voltage. The lamp selected was the PR-13 which is an argon-filled miniature flange based bulb (flashlight style) with design ratings of 4.8V/0.50A/15 hours. A large quantity from the same production lot was procured. The lamps were tested under stationary conditions using direct current and base down positioning. Applied voltage was held to within $\pm 0.01V$ of the test value. Test voltages were 4.80V (100% rated), 5.80V (120.8% rated), and 6.00V (125% rated). Test sample lot sizes were 6, 4, and 9 respectively. The derived life exponent for the increase from 100% to 120.8% of rated was 9.9 and the derived life exponent for the increase from 120.8% to 125% of rated was 10.4. While the sample sizes were fairly small, the data do suggest that at voltages well above rated, the life expectancy will be somewhat better than that predicted by the nominally-used exponent of 12 for life vs voltage.

SWITCHING VOLTAGE-REGULATORS FOR LEAD-ACID BATTERY CHARGERS

Douglas Strait NSS 9707 *

The traditional constant-voltage charger using a linear voltage-regulator IC is unbeatable for simplicity. All that's needed is a voltage divider and an IC such as the LM317 or LM350, and you're in business (see "Mine Lamp Charger" by Ray Cole, *Speleronics* 6 p.8). All linear voltage-regulator chargers have in common the characteristic that at least 1 amp must be input to the regulator for each amp delivered to the battery being charged. The energy associated with the difference between the source voltage and the battery charging voltage is dissipated as heat. This arrangement is fine for most applications.

For charging from car batteries or other energy-limited sources, the 1 amp in for 1 amp out characteristic of linear voltage-regulator chargers can be a liability: Using a linear voltage-regulator charger, a typical car battery in good condition can fully recharge two Wheat(tm)-style batteries (4V, ~15 Ahr) at moderate temperatures without subsequent starting difficulty. Many of us in the real world, however, cave in the wintertime and only replace our car batteries when they will no longer start our vehicles. I have heard a number of reports of vehicles not starting after charging a single Wheat-style battery.

Switching voltage-regulators offer some relief from this problem. Instead of dissipating the energy associated with "excess voltage" as heat, switching regulators convert it to additional current delivered to the battery being charged. Efficiencies of 85% or better are attainable. A 2-cell lead-acid battery charged with current limited to a reasonable value will accept most of the charge at a terminal voltage in the range of 4.40 - 4.50 volts. This means that a switching regulator with an input voltage of 12.0 volts and an efficiency of 85% will deliver $.85 \times (12.0V/4.50V) = 2.27$ amps to the battery being charged for each amp delivered from the 12 volt source. This is a big improvement over the 1-amp-for-1-amp of the linear voltage-regulator charger. The relative advantage of the switching-regulator charger becomes smaller for decreasing differential between the source voltage and the voltage required for charging.

A number of switching-regulator ICs have been introduced over the years. Some, such as the LM494, LM3524, and the LM3578 have low current capabilities and are best used as controllers to drive external power-transistors. By using any of the above ICs with a very low on-resistance P-channel MOSFET such as the IRF9230, efficiencies in the low 90%'s should be attainable. Other ICs such as the LH1605CK and the LM2579 incorporate BJT power transistors capable of delivering several amps at efficiencies of 70-80%.

I was finally moved to upgrade my vehicle charger from linear to switching-regulator technology when my favorite IC company introduced an 8-pin DIP switching regulator that has adjustable output, onboard current limiting, an externally-accessible voltage reference, and will deliver over 1 amp at an efficiency of 85%! This IC is the MAX758 by MAXIM. Their basic circuit from their data-sheet is shown in Fig. 1.

As you can see, it is relatively simple. R2 and R3 determine the output voltage and are chosen per the formula $R2 = R3((V_{out}/1.23)-1)$ where R3 can be any resistance in the 10K to 1M range.

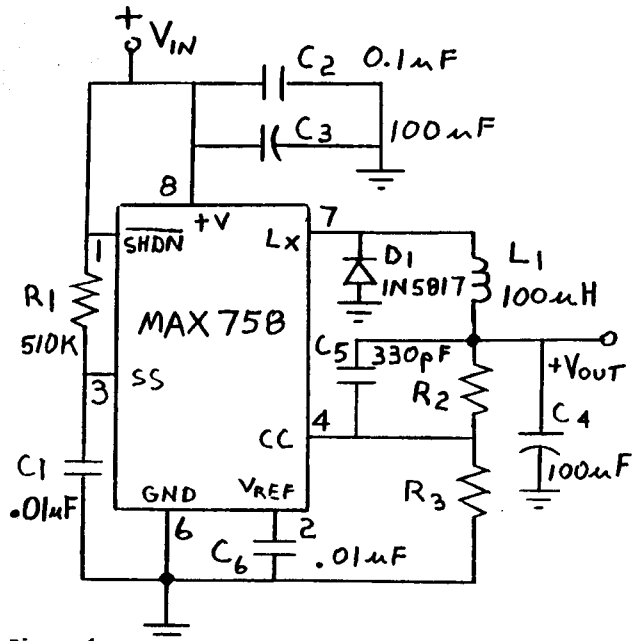


Figure 1.

BASIC STEPDOWN REGULATOR CKT.

I chose to elaborate on their design, as there are several additional things I want from a charger. These requirements are:

1. Indication that it is working.
2. Automatic shift from fast to float-charging voltage.
3. Indication that near-full charge has been attained.

The schematic in Fig. 2 is the version I chose to build.

Operation: The MAX758 is a pulse-width modulated step-down regulator. Pin 4 is the feedback input and the IC regulates to maintain 1.23V at pin 4. The IC has onboard current limiting and the output voltage will sag as necessary to limit output to about 1.1 amp. The lower comparator of the LM393 and R7 perform the function of shifting between the fast and float charging voltages. When the lower comparator output (pin 7) is low, it causes R7 to modify the ratio of the divider formed by R2,3,4 and thus raises the level of Vout to the "fast" charge level. A low output of this comparator also causes the output of the upper comparator to go low, thus causing LED D2 to illuminate to indicate "fast" charge status. As the battery approaches full charge, charging current will taper off to a low value. When the voltage across R8 falls below the threshold established by the divider network consisting of R5 and R6 (R5 and R6 are dividing a 1.23V reference from pin 2 of the MAX758), the comparators will go high. R7 will no longer modify the ratio of the R2,3,4 divider, and the output voltage will fall to the "float" level. The "fast" charging LED, D2, will extinguish. R6 can be varied to vary the current threshold for the fast/float transition. The value of 820 ohms shown will cause the threshold to be about 0.1 amp. Raising the value of R6 will raise the current threshold.

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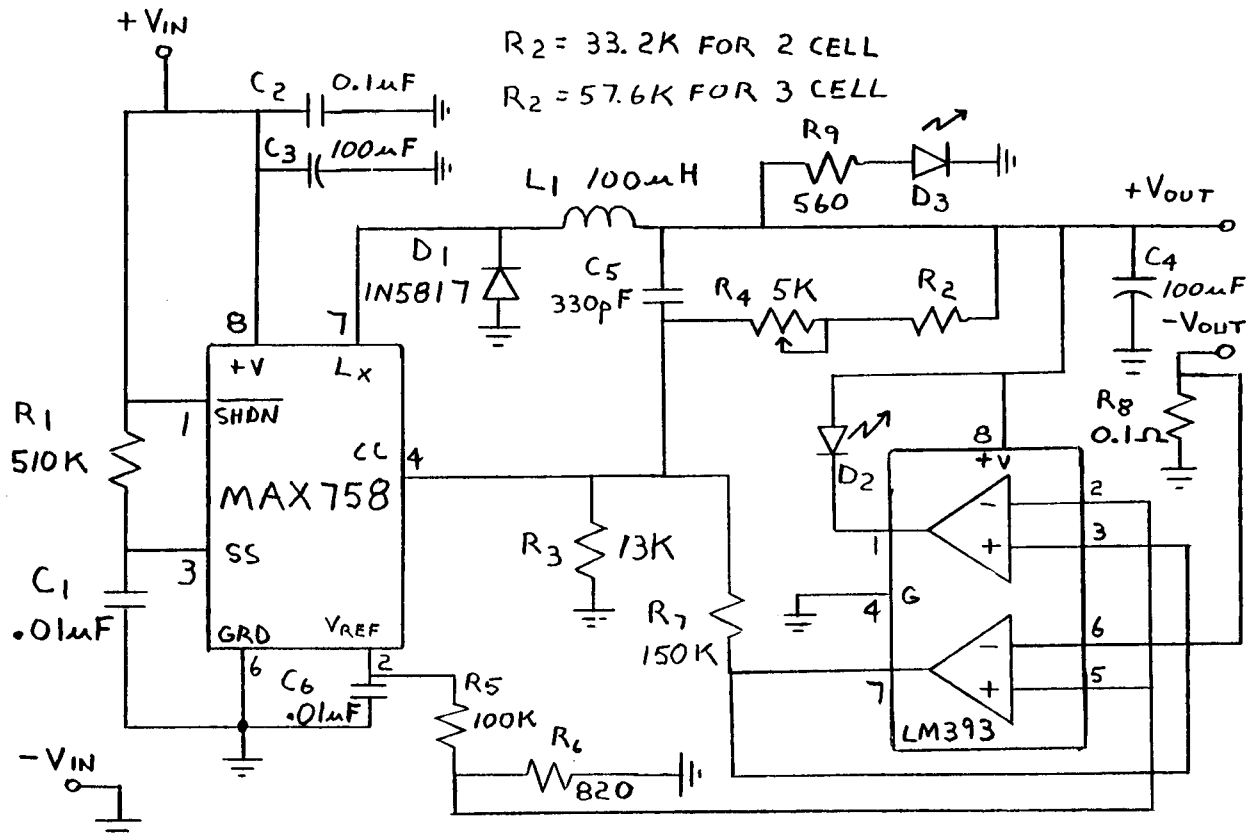


Figure 2.

CHARGER WITH ALL THE TRIMMING S

What is an appropriate threshold? It must be higher than the value the battery-charging current tapers down to while on the "fast" charging voltage. I suggest setting the threshold no lower than C/100 where C is the capacity in AHr of the largest battery you anticipate charging. Wheat Lamp users may consider a threshold of around 0.2 amp. If you tend to have old and/or abused batteries you may wish to set the threshold somewhat above the C/100 minimum, as old/abused batteries tend to have higher residual currents. In general, when the fast-charging LED extinguishes, the battery will be very close to full charge, typically within 1 or 2%. Except at elevated temperatures, the battery could be left on float for weeks without harm. LED D3 is a pilot light which will illuminate either with input power supplied or with a battery connected to the output, thus it can be used to indicate both power availability and continuity from charger to battery under charge.

Perform initial checkout and adjustment as follows: Voltage values are indicated for both 2-cell and (3-cell) versions. With 12V applied to the input and no battery attached to the output, D2 should be extinguished and D3 illuminated. Adjust R4 to obtain 4.60 (6.90) volts at the output. Apply a load to the output slightly above your fast/float transition current. LED D3 should illuminate and the input voltage should rise to 4.80-4.90 (7.20-7.35) volts. Increase load and observe current limiting. Current limiting will typically occur in the range of 1.0-1.2 amps. Reduce load to a low value and observe transition to float voltage and that LED D3 extinguishes. Those who lack suitable equipment to use

as a variable load can improvise by using a fully-charged battery: Remove a few tenths of 1% of charge from the battery by running a light for a few minutes. Then connect your battery and ammeter to the charger. The charger will initially current-limit but charging current will soon taper off, allowing you to observe the "fast" charge voltage level and fast/float transition current. Note that the "fast" level will rise slightly with falling current due to the small voltage drop associated with R8.

Some general comments on construction and component selection: D1 (1N5817) is a Schottky diode. Do not substitute a non-Schottky type. L1 must have a DC current capability of at least 1.1 amp and the knee of its saturation curve should be >1.5 amp. Any value in the range of 80-120µH should be OK. I used 35 turns of 20-gauge [0.081cm dia.] wire wound on a 0.8" [2.03cm] dia. toroidal core which gave me 95µH and a saturation-curve knee at around 5 amps. Values of C1,2,3,4 are not very critical but C2 should be ceramic and ≥0.047µF and C1 should be ≥0.01µF. Locate C2 and C3 electrically close to the MAX758. The MAX758 is a CMOS device so the usual ESD precautions should be exercised during construction. If you use both 2 and 3-cell batteries as I do, you may wish to incorporate duplicate R2 and R4 along with a toggle switch to provide for charging either battery. Input and output connectors should be selected to suit your needs. I used a 5.5mm OD/2.5mm ID DC power plug for the input. Beware of plug/jack designs in which a momentary short is possible when you insert the plug. If the other end is already plugged into your car cigarette

lighter socket it will blow the fuse serving the cigarette lighter.

Note that the design as presented is not reverse-polarity protected on either input or output. I did not require reverse-polarity protection, as both my input and output connector arrangements are polarized, thus precluding error. If your planned output-to-battery connection arrangement is not similarly foolproof and you are not one of those people who never make mistakes, you should consider incorporating reverse-polarity protection for the output. I do not recommend the usual blocking diode solution, as the forward drop thru the diode costs too much in terms of efficiency. The energy-efficient reverse-polarity protection solution is to fuse the output. If a battery is reverse-polarity connected, D1 will be forward biased and the resulting large current will blow the protective fuse. Since the MAX758 will be in current limit most of the time, it will be working pretty hard. Special provision for heat sinking is probably not necessary, but to be on the safe side I glued a 1 square inch [2.54cm] piece of copper to the top of IC to act as a radiator. I assembled the whole works in a plastic box about the size of a pack of cigarettes.

Switching frequency is about 165 kHz. I tested for RFI by holding the charger (under load) near the loop antenna of a broadcast receiver. The charger could be heard on the AM band at distances of \leq two feet [61cm].

How does it perform? My unit is set up to operate as either a 2-cell or 3-cell charger. Current limits at 1.1 amp. With a 12V input, efficiency while in current limit is 85% at 2-cell voltage and 86% at 3-cell voltage. Partial-load efficiencies are slightly better but this is not particularly relevant, as most of the total charging will occur while in current limit. The mean ratio of output to input current over a complete charge is 2.27 for 2-cell and 1.53 for 3-cell. For decreasing input voltage, an output of ≥ 1.0 amp at an output voltage ≥ 4.60 (6.90) volts can be maintained down to an input voltage of 8.7 volts for 2-cell and 11.7 volts for 3-cell.

While this design is not temperature compensated, performance should be adequate in the range of 15°F(-10C) to 80°F(27C). Above 80°F(27C) the specified voltages are a little high and thus the residual charging current may

not fall low enough to trigger the fast/float transition. Those who anticipate routinely charging at temperatures $>80^{\circ}\text{F}(27\text{C})$ should set the float voltage at 4.50 (6.75) which will lower the fast level by a similar amount. If this is done, the lower temperature limit of good performance will be around $32^{\circ}\text{F}(0\text{C})$. Those requiring performance over the widest possible temperature range should temperature-compensate the charging voltage. This is readily done by replacing a portion of R2 with a negative-coefficient thermistor with appropriate value and slope.

Those who would like more bells and whistles might wish to include a 2-step charging level indicator. This is readily done by using a LM339 in place of the LM393. The LM339 is a quad comparator. By adding two additional resistors to the R5/R6 divider network, the additional two comparators could be used to drive LEDs indicating charging current levels of, say, 0.25 and 0.75 amp.

For a MAX758 datasheet:
Maxim Integrated Products
120 San Gabriel Dr.
Sunnyvale, CA 94086
(408) 737-7600

References:

1. Cowlshaw, M.F. "The Characteristics and Use of Lead-Acid Cap Lamps." Transactions of the British Cave Research Association. v.1 no.4, December 1974 p199.

Automatic analog-regulator battery chargers:

2. Cole, Ray "Mine Lamp Charger" Speleonics 6 (v.1 #4, Fall 1986). (Reprint; article also appears in Caving Basics (NSS 1988) and numerous other publications.
3. _____ Sky and Telescope magazine, July 1989 p97.
4. Johnson, Don H. WB6MXD. "A Different Kind of Charger" 73 magazine, Aug. 1980 p115.

H₂ CATALYSIS FOR SEALED STROBES

John Ganter NSS 22870

[Reprinted by author's permission from cavers' computer-mailing list, 20 June 1991.]

There have been reports in the caving literature of strobes and "Weatherproof" cameras exploding (Caves & Caving 44 & 45, reprinted in SPELEONICS 14, also report in #15).

The culprit appears to be hydrogen (H₂) which evolves from alkaline and other "sealed" dry-cell batteries, particularly when they are discharged rapidly. The hydrogen is apparently ignited by sparking at switches or the high-voltage trigger circuit/electrode on the strobe.

Development work on high-powered and re-packaged strobes for caving led to further examination of this problem. I recalled that my Pelilite(™) dive light has a collar around the reflector containing two small cylinders and the label, "Hydrogen absorber. Dry if wet." Efforts to obtain information from Pelilite were unsuccessful.

Inquiries were made to cavers by e-mail, with Frank Reid and Duke McMullen making suggestions for a chemical or catalytic solution. It was determined that MnO₂, while used within dry cells, would not work under ambient conditions.

Rane Curl then suggested a 1% platinum catalyst on alumina pellet substrate, in order to achieve what he termed "H₂-O₂ Recombination Catalysis."

A lengthy and expensive series of phone calls then took place. Eventually, a chemist at a large firm spoke on condition of anonymity. Platinum on alumina works in this application, even at 1/2%.

Provided that sufficient O₂ is present, all H₂ will be consumed and water produced. The chemist refused comment on the number of pellets required.

(Bill Stone has since pointed out that Tekna(™) dive scooters have large platinum catalysts glued inside their housings to absorb H₂ from the vented lead-acid batteries)

The NSS Safety & Techniques Committee has obtained a quantity of the catalyst pellets. They will be used in a ratio of two pellets per C-cell or rough equivalent, with an adjacent desiccant pack to absorb the water produced. The first application is in the "TU-83," a re-packaged (waterproof) Vivitar(™) 283 strobe presently being field tested.

The pellets are available free to any caver or diver who wants to experiment with them in strobes, dive lights, etc. We also have a large quantity of silica gel desiccant which is useful for camera equipment, film storage, electronics, etc.

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See author's address on page 12.

