MEMORY EFFECT IN STATIONARY NI-CD BATTERIES?
FORGET ABOUT IT!

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ABSTRACT

Despite decades of education efforts by the manufacturers of stationary nickel-cadmium (Ni-Cd) batteries, many determined users cling to the notion that these batteries exhibit the memory effect and are therefore not suitable for their application. Such ideas are perpetuated by user perceptions of sealed cylindrical Ni-Cd cells in portable household appliances, in which just about any instance of substandard performance is attributed to memory.

Published literature is not always helpful in dispelling the myth of memory effect in vented Ni-Cd batteries. The book that is widely considered to be the nickel-cadmium 'bible' seems to be curiously silent on the subject. Other reference books are more enlightening, but there is unfortunately also plenty of misinformation available to the unwary reader.

Part of the confusion over the memory effect arises because the term itself is loosely applied to a variety of battery ills, some of which affect more than one electrochemical system. This paper describes several types of battery behavior that fall into this category and defines the "real" memory effect. A summary of the literature on the phenomenon is presented, along with a rundown on the battery types that exhibit it and the operational parameters that cause it.

It is hoped that this information will convince users and potential users of stationary nickel-cadmium batteries that they can indeed forget about memory.

INTRODUCTION - A BRIEF HISTORY OF MEMORY

It took a while for the memory effect to surface. The Ni-Cd battery was patented by Swedish electrochemist Waldemar Jungner in 1899. Many years went by, during which first the pocket plate design, then sintered plates, then sealed Ni-Cd cells were developed. Yet when Falk and Salkind published "*Alkaline Storage Batteries*" in 1969[1], widely considered to be the Ni-Cd 'bible,' they did not mention the memory phenomenon (although there are some related points that will be discussed later).

It was in relation to the space program that the memory effect was discovered. This was sometime in the 60s, and the effect occurred when sealed sintered plate cells on orbiting satellites were subjected to highly repetitive cycles of about 25% depth of discharge (DoD). It was found that if the discharge was continued past the normal point, a voltage dip occurred and the remaining energy could be removed only at a depressed voltage. Although this discovery was made some time before Falk and Salkind went to press, they apparently did not regard the effect as being worthy of inclusion in their book.

In the years since that discovery, however, just about every non-ideal behavior of Ni-Cd batteries has been attributed to 'memory' at one time or another. The memory devotees were given more ammunition in the mid- to late-1980s when the manufacturers of stationary Ni-Cd batteries had to deal with the emergence of the float effect. In addition to explaining this phenomenon and how it affects the operation of these batteries in float applications, the manufacturers had to contend with countless questions from skeptics who believed that the float effect was simply memory disguised under a different name.

Although the battery community as a whole is much more knowledgeable about Ni-Cd than it was 15-20 years ago, such questions have continued at a low but persistent level. It was for this reason that the author decided to write this paper.

PLATE TYPES

A useful introduction to any discussion on memory is an understanding of the plate designs that are used in various Ni-Cd batteries. Many of the phenomena that will be discussed in this paper are either restricted to or influenced by a particular plate construction.

Pocket

This traditional plate construction dates back to the early 1900s and is still in widespread use today for stationary applications, since it is one of the most rugged battery types available. The active materials are held in 'pockets' comprising two perforated steel strips that are crimped together along both sides. A number of pockets are linked together within a steel framework to form each plate. The active materials—nickel-based in the positive and cadmium-based in the negative—are mixed with different additives before being filled into the pockets. The most important of these additives, at least in relation to memory, is an expander—typically a form of iron mass—that is added to the negative material. This expander helps to control the crystalline characteristics of the cadmium active material during cycling.

Sintered

Commonly used in both consumer and aviation batteries, sintered plates offer both high power and comparatively high energy density. This construction is used for both positive and negative plates in many designs, and also for positive plates in some hybrid designs. Nickel powder is sintered (the particles are welded together but not melted) onto a metallic sheet, resulting in a matrix with porosity greater than 80% into which the active materials are chemically or electrochemically impregnated. This results in very uniform filling and good contact with the conducting substrate.

Foam

Foam electrodes are used for the positives of batteries with high energy density, especially nickel-metal hydride. Foamed urethane is nickel-coated, and then the urethane is burned away to leave a nickel framework that consists of 95% void spaces. The nickel active material is physically impregnated into the plate in the form of a paste.

Plastic-bonded

This plate construction is somewhat similar to the sintered design, but with the nickel matrix replaced by a synthetic rubber compound. Plates are produced by coating a slurry of active material, plastic and expanders onto a metallic sheet. Plastic-bonded plates are not suitable for positive electrodes, so their use is restricted to the negatives of hybrid designs, typically with sintered or foam positives.

Fiber

Fiber plates are constructed from a fibrous plastic matrix in which the fibers have been coated with nickel to make them conductive. Active material slurries are vibrated into the void spaces in the matrix to form either positive or negative plates. Additives may be used and in fact it is normal to have a small percentage of expanders in the negative material.

MEMORY AND OTHER PHENOMENA

This section of the paper discusses the memory effect in detail, as well as a number of other phenomena that are sometimes – or even frequently – labeled as memory.

'True' Memory

The memory effect, and at least one of its causes, was very ably described in a paper by Pensabene and Gould in 1976[2]. They discussed the case of a sealed sintered-plate Ni-Cd battery that was subjected to repeated and precisely controlled cycles of 25% DoD, in relation to operation on orbiting satellites with photovoltaic charging. The battery was fully recharged on each cycle, but with no overcharge. After 'a great many cycles,' a continuation of the discharge past the 25% point showed a pronounced voltage step. The residual capacity was available, but only at a reduced voltage. Reference electrode readings showed that the voltage drop occurred at the negative electrode, and scanning electron microscope photos of 'memorized' and normal negative material showed a marked difference in crystal size for the cadmium active material. Figure 1 shows these photographs and the associated discharge curves for 'memory' and 'non-memory' cells.

It is clear that the larger crystals in the negative material of 'memory' cells have a smaller surface area and will therefore be more difficult to discharge. In this partial theory of memory, the 'working' part of the capacity retains its small crystal size, while the inactive part grows into larger crystals. There are two factors influencing the formation of larger crystals. The first is a relatively low charging rate, discussed more fully later in this paper; and the second is the lack of an expander in sintered electrodes. An expander helps to maintain the small crystal size of a healthy negative, but the deposition process for the active materials in sintered plates precludes the use of one.

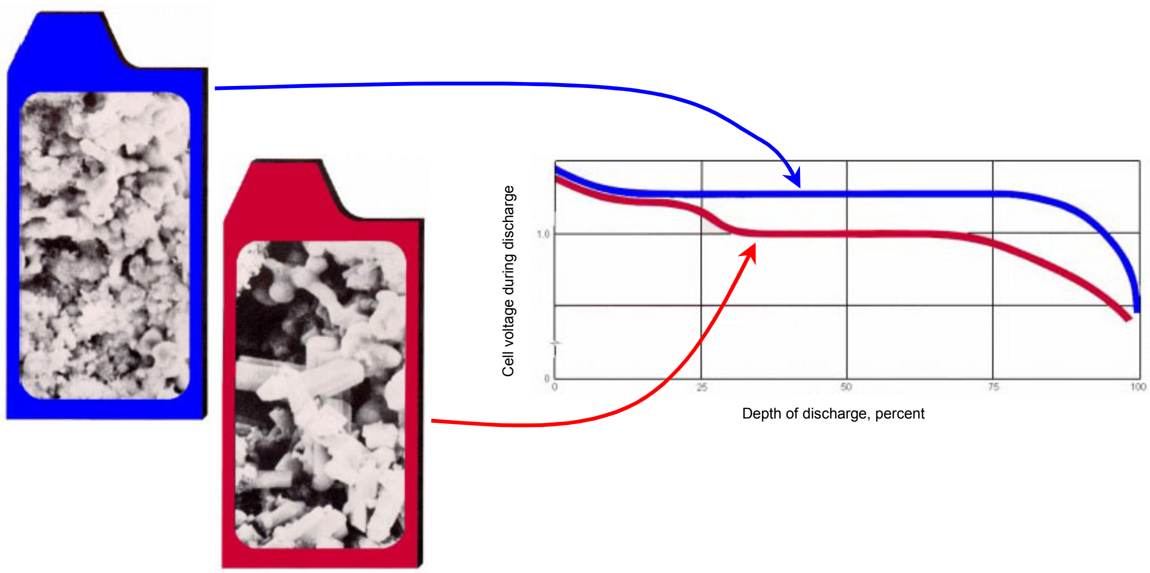

Figure 1 – Normal (top) and 'memorized' (bottom) Ni-Cd cells (from Pensabene & Gould[2])

Another influence is that the negative material goes through a dissolved phase as it transitions between metallic cadmium and cadmium hydroxide on charge and discharge[3]. This promotes crystal growth during cycling of cells that do not contain expanders in the negative material (i.e. sintered negative plates).

Pensabene and Gould also discussed a 'lost contact' theory, in which contact points are lost between the active material and the current-carrying substrate. This subject is also mentioned by Crompton[4]. However, in neither case is there a mechanism proposed for the lost contacts, and it appears likely that this is just another aspect of large crystals of active material.

A more important cause of the memory effect is mentioned by Crompton and discussed in some detail by Berndt[5]. It has been found that cadmium will form intermetallic compounds with the nickel substrate of sintered plates. Compounds like Ni_2Cd_5 or Ni_5Cd_{21} build up under the operating conditions that cause memory; when a complete discharge is carried out, using the cadmium from these compounds causes the voltage to drop by about 150mV. The other plate types do not have the large amount of nickel substrate that is present in sintered plates, so they do not form these compounds. Many now believe this to be the primary mechanism for the memory phenomenon, although it is difficult to separate it completely from the crystalline effects.

It must also be said that it is exceedingly difficult to set up the memory effect. Pensabene and Gould discuss work at GE, in which Ni-Cd cells were subjected to over 5000 charge discharge cycles with no deterioration in performance (although they fail to detail the test conditions). Sato *et al*[6] tried to induce memory with 50 closely controlled partial discharge cycles without success (more on this later).

From this information, it can be seen that the memory effect is not a simple phenomenon, but is established by a rather complex and difficult-to-reproduce process. Nevertheless, it can be stated that true memory is restricted to cells with sintered negative plates and involves both crystalline effects and reactions between cadmium and nickel. The simple cure for this complex phenomenon is to discharge the battery completely, then recharge it normally.

Float Effect and Voltage Depression

Both or these terms describe the same overcharge phenomenon, in which the charged nickel positive material is transformed from the β-form of NiOOH to the γ-form. Both are generally expressed as containing Ni^{3+} ions, but due to the non-stoichiometry of nickel hydroxides the actual oxidation states are around 3.0 to 3.1 for the β-form and 3.5 or more for the γ. γNiOOH has a higher coulombic capacity but the discharge voltage plateau is lower. This is shown in Figure 2, which depicts medium-rate pocket-plate cells discharged at two different rates. In each case, a discharge curve is shown for cells charged in accordance with IEC 60623[7], corresponding to βNiOOH, and ones subjected to prolonged float charging, corresponding to the γ-form.

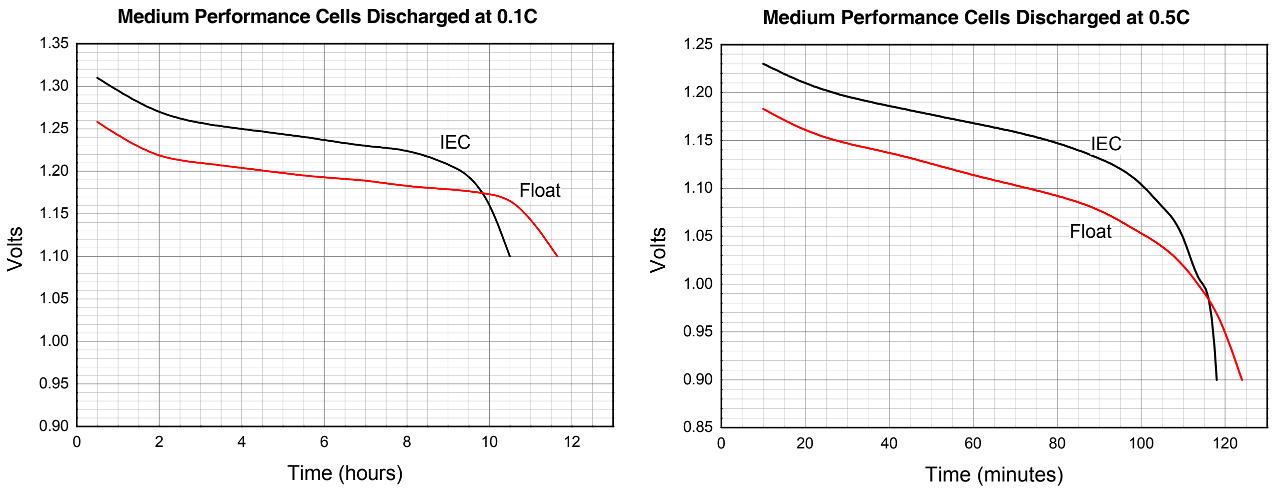

Figure 2 – Float effect in medium-rate cells

Starting from a fully discharged state, initial charging at the standard IEC rate of $0.2C_5A$ (20A per 100Ah of rated capacity) for 7 hours (corresponding to a charge input of 140% of rated capacity) will leave the cells at 100% state of charge and with the positive material as βNiOOH. Continued charging will gradually convert the positive material to γNiOOH, a process that takes a few months in a float application.

From the $0.1C_5A$ discharge curves in Figure 2, it can be seen that the transition between the voltage-limited 'float' curve and the capacity-limited 'IEC' curve occurs between 1.17 and 1.18V/cell—well above the normal end-of-discharge voltage of 1.00-1.14V/cell. In this case the coulombic capacity is actually increased because of the float effect (although the energy is decreased slightly).

When the discharge rate is increased to $0.5C_5A$, however, both voltage curves are lowered and the transition point falls below 1.00V/cell – lower than the minimum allowable voltage for most applications. The available capacity is therefore reduced, with the extent of the reduction depending on the end-of-discharge voltage. For this particular cell and discharge rate, the available run time to a minimum voltage of 1.14V/cell is reduced by more than 50% by the float effect. To a minimum of 1.10V/cell, on the other hand, the reduction is only about 25%.

A word on terminology: 'voltage depression' is a very generic term that could be used to describe any of the phenomena covered in this paper. Most batteries in stationary applications are charged with modified constant potential 'float' chargers, so the term 'float effect' is used and it is less likely to be confused with any other effects. Having said this, the same effect can be induced through overcharging by other means, such as low current 'trickle' charging or even high-rate constant current charging.

The float effect applies to the positive active material itself and is not specific to any specific plate design; nor is any design immune from this phenomenon. Like the memory effect, the float effect can be removed by a complete discharge and recharge. However, this is plainly impractical in a standby application, and the effect would fully reestablish itself within a few months in any case. For this reason, manufacturers of vented Ni-Cd batteries who wish to sell their products for use in float applications must publish performance data that are based on prolonged float charging.

In consumer applications, many users leave cordless appliances in their charging cradles except when the devices are being used. The resulting overcharge is sure to produce the float effect and, depending on the discharge rate and voltage limit, this may affect the operating time. It is highly likely that most users who say they have experienced memory have actually encountered the float effect.

Capacity Fading

Also known as 'ratcheting' or 'walkdown,' capacity fading is a temporary effect resulting from incomplete recharge between successive discharges. This effect is seen predominantly in vented Ni-Cd batteries (as well as vented lead-acid) and can lead to a progressive imbalance between the positive and negative electrode capacities.

During recharge, particularly at higher states of charge, the negative tends to charge at higher efficiency than the positive. If charging is discontinued before completion, the negative will be at a higher state of charge than the positive and the available capacity will be reduced. If this process is repeated, the divergence in state of charge of the two electrodes will become progressively worse with each cycle. This will continue until the incremental charging efficiency of the positive is the same as that of the negative.

Since the primary cause of inefficiency in the positive is oxygen evolution, the recombination process in sealed Ni-Cd cells (as well as in VRLA) tends to limit the disparity between the electrodes. Whenever oxygen is evolved at the positive and recombined at the negative, the net reaction at the negative is zero. However, the oxygen in vented cells escapes from the system and the negative is free to recharge until it is virtually fully charged and hydrogen evolution begins. This factor, combined with the normal overcapacity of the negative electrode, allows the imbalance to occur.

This effect occurs only in cycling operation and can be cured by periodic equalize charging with enough ampere hours being returned to the battery to ensure full charging of both electrodes. It should be noted that the capacity fading mechanism described here is not the same as the so-called 'premature capacity loss' or 'antimony-free' effect that is seen in certain lead-acid designs. This effect is beyond the scope of this paper.

Second Discharge Plateau

This memory-like effect is associated with the positive electrode, but is a very isolated phenomenon. When this effect is present the cell begins discharging normally, but at some point there is a drastic voltage drop from the normal level of approximately 1.2V down to about 0.8V. The voltage stabilizes to produce a second discharge plateau, at which the residual capacity is discharged. This effect is shown in Figure 3.

Sac-Epée *et al*[8] attribute this effect to positive plates with a poor interface between the active material and current collector. Furthermore, they state that the effect is limited to plates that have been physically impregnated, such as pasted foam electrodes, and that it is not seen in sintered plates in which the active material has been electrochemically deposited. Berndt suggests that this effect can be found with sintered positives[9], but it appears that some hundreds of cycles are required to observe it in those designs.

Several mechanisms have been suggested for this effect, such as the establishment of a boundary layer with semiconductor properties; a loss of contact between the active material and the substrate; the formation of a low-energy form of βNiOOH; and phase transitions between γNiOOH and $\beta Ni(OH)_2$. One of the most recent papers on this subject is by Léger *et al*[10], who suggest that the effect is caused by a poorly conductive phase of the discharged active material that is in close proximity to the current collector. Unlike the true memory effect, the second discharge plateau can be seen on the first discharge of an affected cell. Cycling does worsen the effect, however, and capacity is gradually transferred from the usable first plateau to the unusable second plateau.

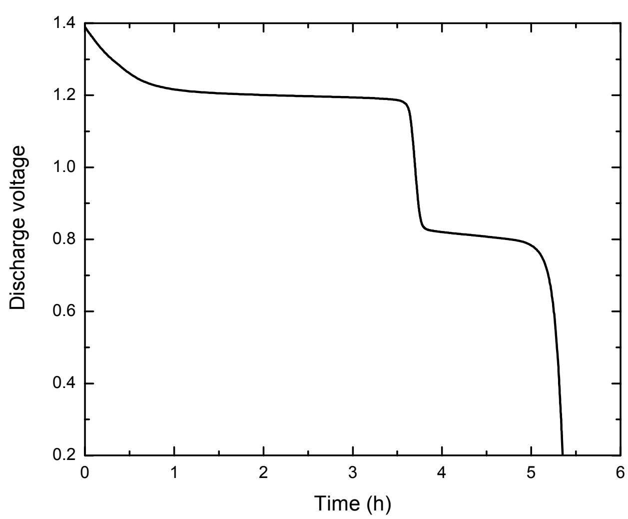

Figure 3 – Second Discharge Plateau

As mentioned previously, the second discharge plateau is an isolated phenomenon, certainly with respect to stationary applications. It is also entirely different from the float effect, in which no voltage step is apparent.

Coup de Fouet

While on the topic of voltage steps, dips and depressions on discharge, it is worth mentioning the initial voltage dip, or coup de fouet, that occurs in lead-acid batteries. Coup de fouet (pronounced '*coo duh fway*') is French for 'crack of the whip,' and it is seen as a sharp voltage dip in the first seconds or minutes of a discharge. This is followed by a partial recovery up to the normal plateau of the discharge voltage curve.

In lead-acid batteries, the coup de fouet effect is seen during the initial discharge of a positive electrode in which no lead sulfate is already present. Pb^{2+} ions form a supersaturated solution at the plate surface, until the initial 'critical seed' crystals of lead sulfate are formed. Bode[11] suggests a voltage dip of 20mV or more until enough seed crystals have been formed and the oversaturation disappears.

The coup de fouet phenomenon is a function of the dissolved phase transition between the charged lead oxide and the discharged lead sulfate and does not occur in Ni-Cd cells.

CHARGING ISSUES

Having described what the memory effect actually is (and is not), this section of the paper will discuss ways in which variations in the charging process can enhance or prevent the formation of this and the other effects.

Charging Rate

Those who remember growing crystals in the chemistry lab in school will be aware that large crystals take time to form. Crystals that are produced quickly are invariably rather small and fragile. The same is true for charging. Fast charging produces small crystals that have a large surface area-to-volume ratio and can be easily discharged. Slow charging favors the formation of larger crystals, unless other factors intervene, such as the presence of expanders in the negative active material.

It takes more than just slow charging to form memory, but a low charging rate certainly increases the chances of producing the effect. It has already been established that only sintered negative plates are vulnerable to memory, and Falk and Salkind state that the charging efficiency of the negative electrode in sealed sintered plate cells increases with increasing charge rate, up to $1.0C_5A$[12]. (Interestingly, they also say that the highest charge efficiency for the negative is when the previous discharge was at a high rate and the crystals of cadmium hydroxide thus produced are small.)

For portable applications, memory is essentially non-existent for devices using fast chargers with thermal cutoffs, as in many power tools. Although trickle chargers for cordless phones and similar appliances charge at low rates, 'true' memory would be generated only if the usage pattern is highly (and precisely) repetitive.

Charging Temperature

In common with other battery systems, Ni-Cd batteries show a reduction in available capacity at low temperatures and a reduction in operating life at high temperatures (although the rates of change for these effects vary from system to system). In addition, Ni-Cd batteries show reduced charging efficiency at high temperature due to effects on the positive electrode. Although this effect is normally unimportant in a float application, it can have an impact when charging time, voltage and/or current is limited, either by equipment or by specification. For example, some telecom systems have a specification requirement to recharge at the float level to a minimum percentage of capacity within 24 hours. For Ni-Cd batteries, this may lead to a recommendation that temperature compensation of charge voltage be deactivated, as discussed by Lansburg *et al*[13].

In a cycling application with limited recharge time, high operating temperature could lead to incomplete recharge, which in turn can cause capacity fading as described earlier in this paper.

Undercharging

Undercharging may result from limitations in charging voltage, current or time, or from limited charging at high temperature, as discussed in the preceding topic. Repeated undercharging in a cycling application will lead to capacity fading.

Overcharging

As discussed previously, overcharging is the primary cause of the float effect in Ni-Cd batteries. Any form of charging that results in a charge input of more than around 200% of discharged capacity (the exact figure depends on temperature, charge rate and time), compared to 140% for 'optimum' recharge, will generate some γNiOOH. In the previously mentioned paper by Sato *et al*[5], they attempted to produce memory by performing partial discharges, but then they recharged their cells as if they had been fully discharged, thus overcharging them. The cycling was not sufficient to generate memory, but the overcharging clearly induced the float effect, with a slightly depressed voltage plateau but increased capacity. X-ray diffraction tests found the presence of γNiOOH, as should be expected. They correctly said that this was not the classic memory effect, but then mistakenly attributed it to a precursor of memory.

MISINFORMATION

Technical papers in respected journals are not the only source of misleading information about the memory effect. For the serious student of misinformation, the mother lode of deceptive claims and false facts has to be the World Wide Web. The following is a small collection of Ni-Cd 'urban legends' turned up by a quick Google search:

- Memory effect – "A property of NiCad Batteries in which the amount of charging they accept at one time fixes the maximum amount of charging they can accept in subsequent recharges." –*Compact American Dictionary of Computer Words, by Houghton Miflin Company*
- "Always fully discharge your battery before recharging it, this exercises all of the cells in the battery so they are less likely to build dendrides *[sic]*, which are the cause of "memory effect"."
  "Memory Effect- battery loses capacity and begins to use only the cells that are fully charged and discharged regularly…"
  "Do not leave the battery on the charger for extended periods of time, this causes cells to "boil" and will quickly ruin a battery."
  –UC Berkeley, Communication & Network Services, Battery Care & Tips
- Memory effect – "The accumulation of gas bubbles on battery cell plates of a battery that has only been partially discharged before recharging, a bubble reduces the plate area within the battery and thus capacity."
  –Digital Photography Review
- "NiCd batteries are extremely sensitive to "memory effect" build up."
  "If a battery is discharged to 30% and then recharged, the battery will only charge to 30% of its capacity thus shrinking the battery's capacity." *–MobilizeNOW.com*

It must be said that there is also a wealth of accurate information on memory that is available on the Web. The not-so-easy trick is to separate the good from the bad. If there is any doubt, the best course is to obtain as much corroborating evidence as possible, or talk to someone in the technical support department of a major manufacturer.

SUMMARY

In conclusion, it can be seen that the true memory effect is found only in sealed cells with sintered negative plates, and even with those cells it is extremely difficult to reproduce. None of the Ni-Cd batteries commonly sold into the stationary market feature this design, and therefore none of them will exhibit memory.

Of the other phenomena that are sometimes confused with memory, only the float effect is commonly seen in stationary standby applications. Manufacturers must take the float effect into account and publish data based on prolonged float charging for successful operation in these applications, as called out in IEEE 1106[14] and IEEE 1115[15]. In cycling applications, an understanding of the charging process and temperature effects can be used to optimize charging and avoid capacity fading.

It must be said that a lack of understanding about the phenomena of float effect and capacity fading, along with misinterpretation of test results, can and does lead some users to replace Ni-Cd batteries unnecessarily. One thing is certain, however—whatever problem those users think they may have with their stationary Ni-Cd batteries, it isn't memory!

It is more than likely that misinformation about the memory effect will continue to circulate, no doubt aided by uninformed producers of Web pages. Contrary to the urging in the title of this paper, it is hoped that Battcon attendees will not actually forget about memory, but will use this information to educate others about the reality of this over-hyped phenomenon.

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