Handbook and Application Manual

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Introduction

Since its commercial introduction in 1959, the Alkaline-Manganese Dioxide battery has advanced to a dominant position in the portable battery market. This came about because the alkaline system is recognized to have several advantages over carbon zinc type batteries. Some of these advantages of alkaline chemistry over the basic carbon zinc chemistry are:

- Higher energy density
- Superior service performance at all drain rates
- Superior cold temperature performance
- Lower internal resistance
- Longer shelf life
- Greater resistance to leakage

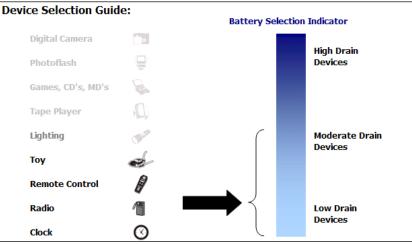


1957 PROTOTYPE Alkaline Battery

Energizer® alkaline batteries are available in a wide variety of sizes to fit most applications. Multiple grades of batteries are also available in the more popular battery sizes. For example the alkaline AA/LR6 size battery is offered in Economy (fig. 1), Standard (fig. 2) and Premium (fig. 3) grades. Each of these grades of alkaline batteries is designed to maximize price and performance for a particular segment of electronic devices.

Energizer® Economy Alkaline:

Designed for long-lasting power for devices with low to moderate drain rates at an affordable price. For example: radios, remote controls and clocks.



(fig. 1) Energizer® Economy Alkaline Selection Guide

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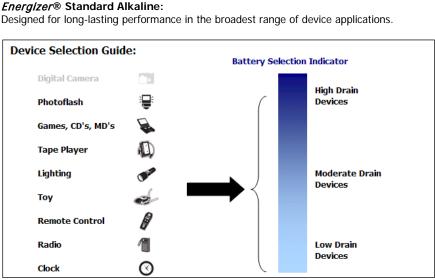
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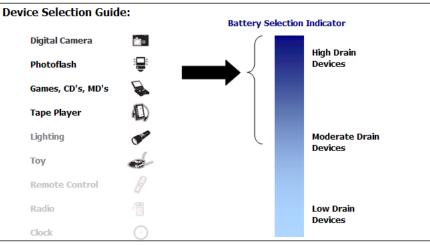
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(fig. 2) *Energizer*® Standard Alkaline Device Selection Guide

Energizer® Premium Alkaline:

Designed to deliver superior run time for high-tech devices. For example: Digital cameras, MP3 players, and hand held games.



(fig. 3) Energizer® Premium Alkaline Device Selection Guide

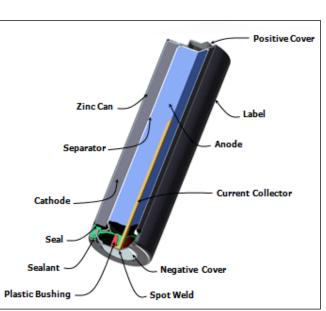
Battery Description

Cylindrical alkaline batteries are produced with a high surface area zinc anode, a high density manganese dioxide cathode, and a potassium hydroxide electrolyte. A cutaway (fig. 4) of a typical cylindrical alkaline battery is illustrated in the following diagram:

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Cathode is a mixture of high purity electrolytic manganese dioxide and carbon conductor. **Anode** is a gelled mixture of zinc powder and electrolyte.

Separators of specially selected materials prevent migration of any solid particles in the battery.

Steel can confines active materials and serves as the cathode collector.

Brass collector serves as the anode collector.

Positive and negative covers provide contact surfaces of nickel-plated steel.

Non-conductive plastic film label electrically insulates the battery.

Nylon seal provides a safety venting mechanism.

Electrochemistry:

An alkaline battery produces electricity when the manganese dioxide cathode is reduced and the zinc anode becomes oxidized. The equation for a simple alkaline cell reaction is as follows:

 $Zn + 2MnO_2 + H_2O \rightarrow ZnO + 2MnOOH$

During this reaction, water (H_2O) is consumed and hydroxyl ion (OH⁻) are produced by MnO_2 cathode under following reaction:

 $2 \text{ MnO}_2 + 2 \text{ H}_2\text{O} + 2 \text{ e} \rightarrow 2\text{MnOOH} + 2\text{OH}^-$.

At the same time, the anode is consuming hydroxyl ions and producing water:

 $Zn + 2 OH \rightarrow ZnO + H_2O + 2 e.$

The electrons (e) generated during the reaction are used to power devices. The rate of the reaction is dependent on the quality of the raw materials and availability of water and hydroxyl ions during reaction. A battery is designed to keep the cathode and anode separated to prevent the reaction from occurring. The stored electrons will only flow when the circuit is closed. This occurs when the battery is placed in a device and the device is turned on. This principle is the same as turning on and off a light switch in a house.

When the circuit is closed, the stronger attraction for the electrons by the manganese dioxide will pull the electrons from the zinc anode electrode through the wire in the circuit to the cathode electrode. This flow of electrons through the wire is electricity and can be used to power applications.

Alkaline batteries typically have a sloping discharge curve. Most devices are designed to operate within a voltage range (for example from 1.6 volts to 0.9 volts per cell) to accommodate this sloping discharge characteristic. The sloping discharge in alkaline batteries is primarily due to the increase in battery internal resistance due to reaction byproducts forming on the electrode surfaces and decrease availability of the fuels (i.e., water). Hydrogen gas is a byproduct of the chemical reaction in all alkaline batteries.

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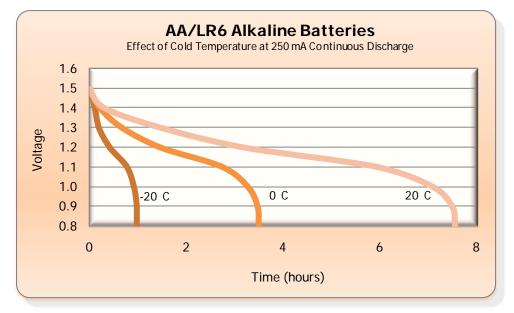
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Under normal usage, this gas production is very low.

However, in abusive conditions, (i.e. charging or electrically shorting) high levels of hydrogen can be produced with larger battery sizes having a greater capacity to generate hydrogen gas. In devices that use a tightly sealed battery case (i.e. diving lights), the hydrogen gas can mix with air to create an explosive atmosphere. For devices with tightly sealed or water proof battery compartments, hydrogen gas generation under normal or abusive conditions needs to be addressed as a potential safety issue to prevent the accumulation of dangerous levels of hydrogen gas within the device.

Temperature Effects on Performance:

The recommended operating temperature range for alkaline batteries is -18° C to 55° C. However, it is important to keep in mind that battery performance is still impacted by temperature within the recommended range. Performance of the battery is primarily dependent on how fast critical fuels, water and hydroxyl ions, can move and react in the battery. The mobility of ions is known as diffusion. For example: maximum battery performance will not be achieved at cold temperatures. As the temperature decreases, the diffusion of the fuels will decrease resulting in lower performance. Batteries will discharge more efficiently as the operating temperature is increased due to increase diffusion of the fuels. As the temperature is decreased, performance decreases accordingly. The lower temperature limit is determined in part by the temperature at which the electrolyte freezes. The Alkaline-Manganese Dioxide cell can operate at temperatures as low as -20°C however this performance will be significantly lower (fig. 5). The operating range for these cells is wider than for Leclanché cells.



(fig. 5) Temperature impact on battery performance

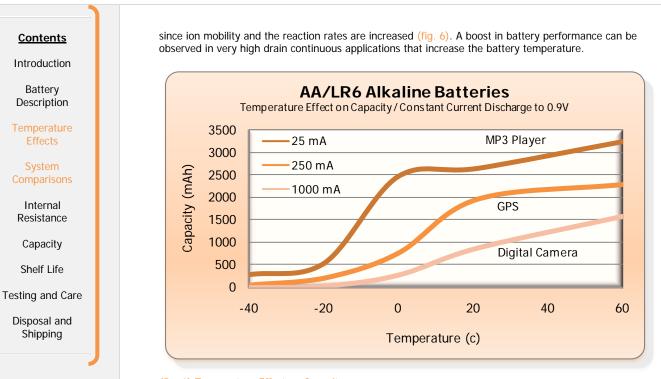
Cold temperatures and their subsequent slowing of the chemical kinetics reactions impact the internal resistance (Ri) of the cell. High drain rates in cold environments will cause a large voltage drop due to the higher battery Ri. Applications using high drain rates (i.e. digital cameras) will be impacted more by cold temperatures than will light drain devices (i.e. MP3 players).

No capacity is actually lost due to cold temperatures; rather it is more difficult to access the full potential of the battery due to the slowing of the electrochemical reactions.

As an example: if a flashlight is stored in a car on a very cold night, the flashlight would not be as bright or last as long when used. However, if this flashlight is taken indoors and allowed to warm up for several hours, its performance would return to normal. Warm temperatures can increase battery performance

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(fig. 6) Temperature Effect on Capacity

Temperature cycling between extreme high and low temperatures can cause expansion and contraction of the battery components. Over time, extreme temperature cycling can cause a failure of the battery seal integrity thereby increasing the potential for leakage.

Comparison to other Chemical Systems:

Various materials can be used for battery components. Batteries using different materials will have different characteristics. For example: voltage, shelf life, temperature effects etc. The following graph (fig. 7) shows the relative performance of three chemical systems versus AA/LR6 batteries at three constant current drain rates. Alkaline performance is being used as a base (100%) with the Lithium and Nickel Metal Hydride (NiMH) performance is represented as a percentage of standard alkaline.





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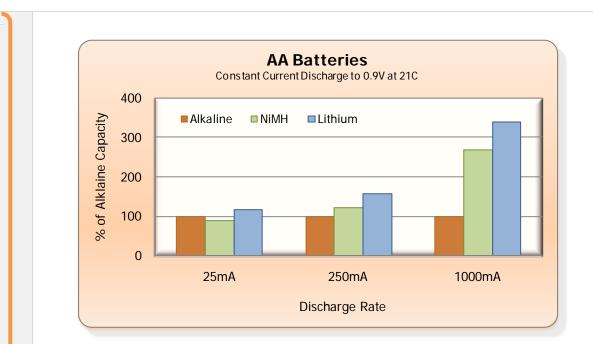
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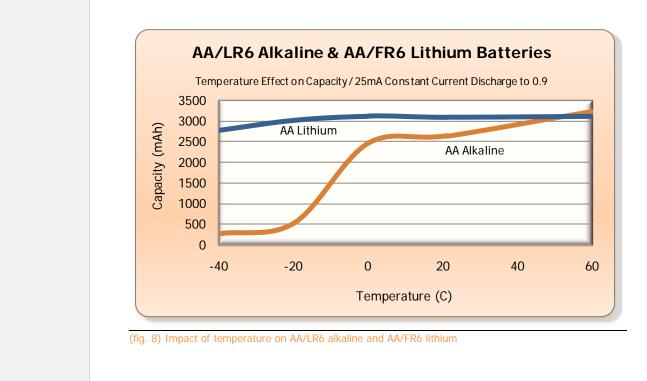
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(fig. 7) Relative performance of three chemical systems with alkaline at 100%

The following graph (fig. 8) shows the impact of temperature on AA/LR6 alkaline and AA/FR6 lithium performance under a 25mA drain rate to 0.9 volt cutoff.



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Internal Resistance:

The internal resistance (Ri) of a battery is defined as the opposition to the flow of current within the battery. There are two basic components that impact the internal resistance of a battery; electronic resistance and ionic resistance. The electronic resistance plus the ionic resistance will be referred to as the total effective resistance.

The electronic resistance encompasses the resistivity of the actual materials such as metal covers and internal components; as well as, how well these materials make contact with each other. The effect of this portion of the total effective resistance occurs very quickly and can be seen within the first few milliseconds after a battery is place under load.

Ionic resistance is the resistance to current flow within the battery due to various electrochemical factors such as, electrolyte conductivity, ion mobility and electrode surface area. These polarization effects occur more slowly than electronic resistance with the contribution to total effective resistance typically starting a few milliseconds or more after a battery is placed under load.

A 1000 Hz impedance test is also used to represent internal resistance. Impedance is defined as resistance to AC current flow. Due to the high speed of a 1000 Hz test, a portion of the ionic resistance factors may not be fully captured. Typically, the 1000 Hz impedance value will be less than the total effective resistance value for the same battery. An impedance test across a range of frequencies is recommended to accurately portray internal resistance.

The impact of electronic and ionic resistance can be observed using a dual pulse test. This test involves placing a battery on a low background drain allowing it to first stabilize and then pulsing it with a heavier load for approximately 100 milliseconds.

Using "Ohms Law" (Volts = Current x Resistance), the total effective resistance is subsequently calculated by dividing the change in voltage by the change in current.

As an example (fig. 9), if a 5 mA stabilization load is used in combination with a 505 mA pulse, the change in current is 500 mA. If the voltage changes from 1.485 to 1.378, the delta voltage would be 0.107 Volts, thus yielding a total effective resistance of 0.107 Volts / 500mA or 0.214 Ohms (214 milliohms).

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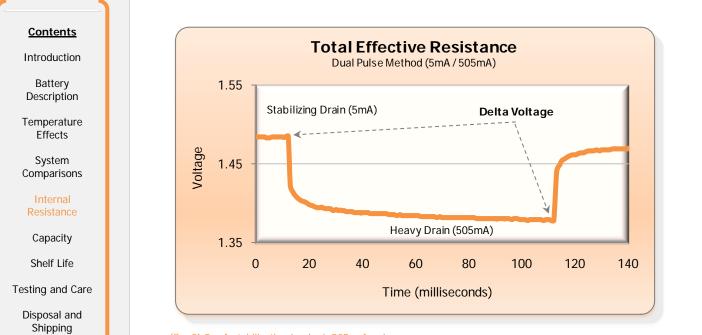
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(fig. 9) 5 mA stabilization load / 505 mA pulse

The typical effective resistance of fresh *Energizer*® alkaline cylindrical batteries (using a 5 mA stabilization drain followed by a 505 mA 100 millisecond pulse) will be approximately 150 to 300 milliohms, depending on size.

The effective resistance of a battery will change as the battery is discharged. The drain rate that the battery is discharged at will effect this change in resistance. Typically, a high drain will result in a relatively low resistance. Low rate discharges will result in a more gradual increase in resistance throughout life of the battery. By continually discharging a battery with periodic high current pulses, the resistance can be calculated through the life of the battery.

The following is an example of an *Energizer*® AA/LR6 alkaline battery being discharged at 50 mA with 10 mA / 500 mA 1 second pulses every 12 minutes. The brown line indicates the voltage discharge curve. The orange dashes are the calculated resistance (delta volts \div delta current) which corresponds to the secondary Y axis on the right hand side of the graph (fig. 10).



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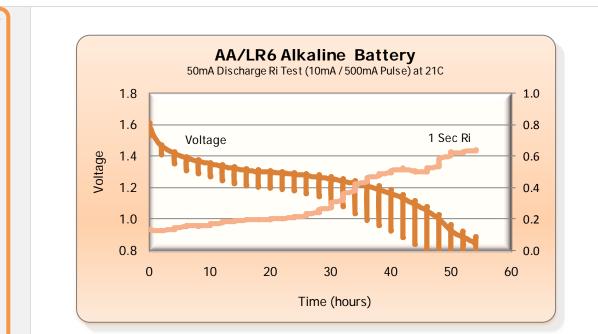
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(fig. 10) Internal Resistance change as battery is discharged.

Flash Amps can also be used to provide an estimate of internal resistance. Flash Amps are defined as the maximum current a battery can deliver for a very short period of time. This test is typically performed by electrically shorting a battery with a 0.01 ohm resistor for approximately 0.2 seconds and capturing the closed circuit voltage. The current flow through the resistor can be calculated using Ohms Law and dividing the closed circuit voltage by 0.01 ohms. The open circuit voltage (OCV) prior to the test is divided by the Flash Amps to obtain an estimate of internal resistance. Since Flash Amps can be difficult to accurately measure and OCV is dependent on many factors, this measurement technique should only be used as a general estimate of internal resistance.

The voltage drop of a battery under load is a function of total effective resistance and current drain rate. An estimate of initial voltage drop under load can be calculated by multiplying the total effective resistance by the current drain placed on the battery.

Example: A 1 Amp drain is placed on a battery with a Ri of 0.1 Ohms. 1.0 Amps X 0.1 Ohms = 0.1 Volts Open circuit voltage = 1.6 Volts 1.6 Volts - 0.1 Volts = 1.5 Volts (expected closed circuit voltage)

In general, internal resistance will rise during discharge due to the byproducts of active materials that have been used. However, the rate of change during discharge is not consistent. Battery chemistry, depth of discharge, drain rate and the age of the battery can all impact internal resistance during discharge.

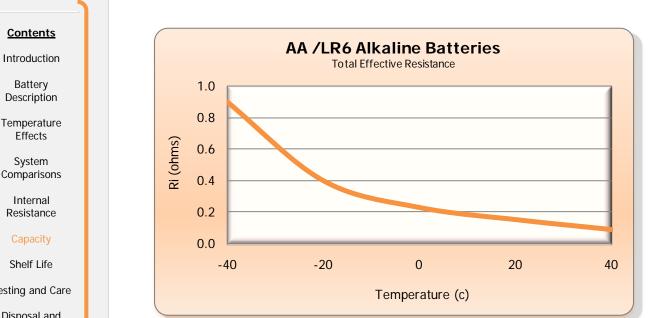
Cold temperatures cause the electrochemical reactions that take place within the battery to slow down and will reduce ion mobility in the electrolyte. Subsequently, effective resistance will rise as ambient temperatures drops. Conversely, as temperatures rise, the electrochemical reactions within the battery become more efficient and effective resistance can decrease.

The graph (fig. 11) shows the effect of temperature on the total effective resistance of a fresh *Energizer*® AA/LR6 alkaline battery.



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(fig. 11) Effect of temperature on the total effective resistance

In summary, internal resistance can be calculated based on the voltage drop of the battery under a known load. Results will be affected by technique, settings and environmental conditions. The internal resistance of a battery should be viewed as a general guideline and not as a precise value when applying it to the expected voltage drop in a specific application.

Capacity:

Battery capacity is typically expressed in terms of milli-Amp hours (mAh). This is an indication of how long a battery will provide service at a specific drain rate to a specific cutoff voltage. For example: the following discharge curve (fig. 12) is an AA/LR6 alkaline battery being discharged at 100mA to a 0.8 volt cutoff.



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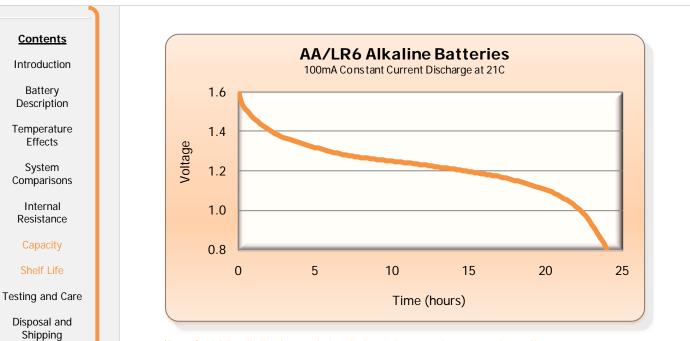
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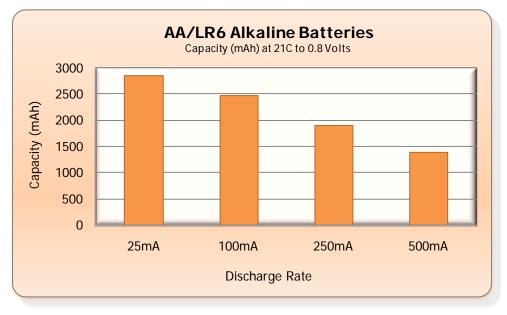
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(fig. 12) AA/LR6 alkaline battery being discharged at 100mA to a 0.8 volt cutoff

The available capacity can then be calculated by multiplying the drain rate (mA) by the hours to the cutoff voltage. For example: this AA/LR6 battery would have a capacity of (100mA X 25 hours) 2500 mAh under a 100mA drain to a 0.8 volt cutoff. The capacity to a 1.2 volt cutoff for this AA/LR6 battery under the same 100mA drain would be (100mA X 15 hours) 1500 mAh.

The mAh capacity of alkaline batteries will vary with the drain rate and the cutoff voltage. In general, batteries are more efficient at lower drain rates. As can be seen on the following bar chart (fig. 13), the AA/LR6 alkaline capacity is far greater at a 25mA drain than at a 500mA drain.



(fig. 13) AA/LR6 alkaline battery capacity to 0.8 volts

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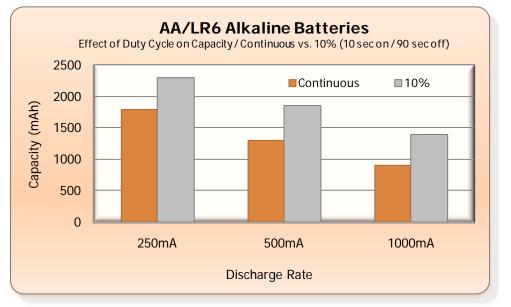
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Disposal and Shipping The application cutoff voltage will also impact the battery capacity. The higher the device cutoff voltage, the more of the battery's capacity will be left in the battery unused. However, a minimum voltage cutoff of 0.8 volts per cell due to the increased chance of excessive internal gassing when alkaline batteries are deep discharged. When the battery has been discharged to 0.8 volts, approximately 95% of the batteries usable capacity has been removed.

In pulse applications, the duty cycle can impact battery capacity. A very light duty cycle will typically allow the battery time to recover and extend service versus a continuous drain. The major contributing factor to this recovery is the migration of active materials within the battery into the reaction area thereby replacing depleted materials and reaction byproducts. The amount of additional service will depend on the drain rate, and the duty cycle (ON time and OFF time of the pulse). Actual testing is needed to determine the amount of additional service expected in pulse applications since there is no simple equation to accurately calculate the impact of duty cycle on service.

The following (fig. 14) are test results of AA/LR6 alkaline batteries at three different drain rates comparing continuous vs. a 10% duty cycle (10 sec. ON / 90 sec. OFF) to a 0.9 volt cutoff.



(fig. 14) AA/LR6 alkaline battery effect of duty cycle

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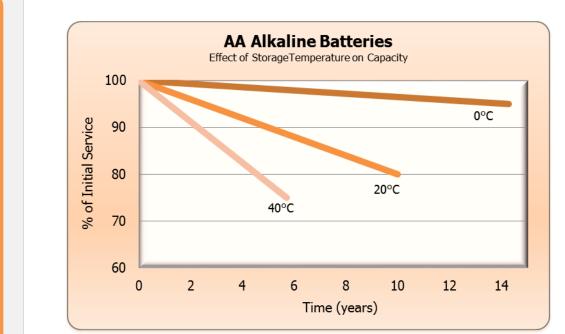
The recommended storage temperature for alkaline batteries is -40° C to 50° C.

Cylindrical alkaline batteries will lose approximately 3% of their capacity per year when stored at 20° C due to slow electrochemical reactions that continually occur. Cold temperatures will slow these reactions down and warm temperatures will increase these reactions.

The following graph (fig. 15) shows the impact of storage temperature on battery capacity.

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(fig. 15) Impact of storage

Testing / Care / Warnings:

Testing:

Measuring the open circuit voltage (OCV) of a battery to determine the amount of service life remaining can be misleading and at best will only yield a rough estimate. A more accurate method is to measure the closed circuit voltage (CCV) of the battery. This is accomplished by placing the battery under load for one to two seconds and measuring the CCV. The load is determined by the size and type of battery. In the case of a single cylindrical 1.5 volt alkaline battery, the load would be approximately 10 ohms. A fresh (unused) battery will typically test at about 1.5 volts CCV. A battery that tests at 1.1 volts CCV has approximately 20% service remaining.

The use of commercially available battery testers to determine the relative condition of a battery. Battery testers are specifically designed for this purpose and have the load and voltage calibrated for different chemistries and battery sizes.

Care And Handling Do's:

The following are recommendations that should be followed to obtain maximum battery performance.

- Do read the instructions on your device before installing batteries. Make sure to insert the batteries properly, following the symbols showing you the correct way to position the positive (+) and negative (-) ends of the batteries.
- Do replace batteries with the size and type specified by the device's manufacturer. Remove all used batteries from the device at the same time, and then replace them with new batteries of the same size and type.
- Do store batteries in a cool, dry place at normal room temperature. Remove batteries from devices that will be stored for extended periods.
- Do inspect devices battery compartment every few months to be sure batteries are not leaking.

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Care and Handling Don'ts

The following are recommendations that users should follow to prevent problems or situations that could lead to personal injuries.

- Don't carry loose batteries in a pocket or purse with metal objects like coins, paper clips, etc. This could potentially short-circuit the battery, generating high heat. When unpacked batteries are mixed together, they can easily short-circuit each other, particularly button-type batteries.
- Don't recharge a battery unless it is specifically marked "rechargeable." Attempting to recharge a primary (non-rechargeable) battery could result in rupture or leakage.
- Don't use rechargeable batteries in chargers that are not designed for the specific battery type.
- Don't put batteries or battery-powered devices in hot places elevated temperatures increase the self-discharge of batteries.
- Do not dispose of batteries in fire.
- Don't mix old and new batteries, or mix different types or makes of batteries. This can cause rupture or leakage, resulting in personal injury or property damage.
- Don't crush, puncture, take apart batteries or otherwise damage batteries. This can cause rupture or leakage, resulting in personal injury or property damage.
- Keep batteries out of reach of children.

Warnings:

Charging of Primary Batteries:

Charging of primary batteries may cause explosion or leakage which may result in bodily injury. IF ENERGIZER/EVEREADY PRIMARY BATTERIES ARE SUBJECTED TO ANY FORM OF RECHARGING, ALL WARRANTIES, EXPRESSED OR IMPLIED, INCLUDING BUT NOT LIMITED TO THE WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, ARE NULL AND VOID.

Metal-Jacketed Batteries

It is important to note that some batteries have metal jackets. Proper design of devices using these batteries should include electrical isolation of the battery jacket from the device circuitry to prevent short circuiting. Short circuits may cause battery leakage which may result in bodily injury.

Plastic Film Labels

It is important to note that some batteries have plastic film labels over the metal can. Proper design of devices using these batteries should include electrical insulation as well as the avoidance of burrs and/or sharp edges and corners that can cut through the plastic and result in battery shorting or inadvertent charging.

Design and Safety Considerations

Click here for the Design and Safety Considerations Interactive on-line Catalog There are many other conditions to avoid for the proper safe use of batteries. It is imperative to read the section "Design and Safety Considerations" to assure that other safety considerations are not overlooked.

Alkaline Manganese Dioxide Handbook and Application Manual

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Disposal and Shipping:

Disposal:

Energizer® standard alkaline batteries are United States Resource Conservation and Recovery Act (RCRA) non-hazardous waste.

Waste standard alkaline batteries meet the United States Federal definition of a solid waste per 40 Code of Federal Regulations (CFR) 261.2. As such, the generator must make certain determinations relative to the waste material. Waste standard alkaline batteries do not fall under any of the specific United States Federal RCRA F, K, P or U lists.

This leads us to the RCRA characteristic waste criteria. Some Toxicity Characteristic Leaching Procedure (TCLP) listed materials may be present in minute quantities in the raw materials, but are well below the established regulatory maximum values. Waste carbon zinc and standard alkaline batteries are not RCRA toxic. Only the characteristics of ignitability, corrosivity and reactivity remain as possible classifications.

The batteries are solid, not liquid, which precludes their being a corrosive waste, since corrosive waste must be liquid by definition. As an inert solid, flash point is not an appropriate test for ignitability. *Energizer*® batteries are a safe consumer product and, under standard temperature and pressure conditions, will not cause fire through friction, absorption of moisture, or spontaneous chemical changes. The batteries contain no sulfides or cyanides, and they do not meet any other reactivity criteria.

United States Federal hazardous waste regulations are specific about relating waste determination to the waste as generated. As generated, scrap standard alkaline batteries are not a specifically listed waste stream and they do not meet the criteria for ignitable, corrosive, reactive or toxic wastes. Scrap standard alkaline batteries are not hazardous waste and they are not regulated by the United States Department of Transportation (DOT) as hazardous materials.

Other nations and some US states may regulate waste based on additional criteria or different test protocols. The status of scrap standard alkaline batteries should be confirmed in the nation or US state(s) where disposal occurs.

Shipping:

The transportation of *Energizer*® alkaline dry cell batteries produced and/or imported by *Energizer*® Battery Manufacturing, Inc. are not regulated as Dangerous Goods by the U.S. Department of Transportation (DOT), the International Air Transport Association (IATA), the International Maritime Dangerous Goods code (IMDG), or the International Civil Aviation Organization (ICAO).

The batteries and their packaging must be protected at all times from direct sun and any sources of moisture, such as rain or wet flooring. Shock and vibration shall be avoided by ensuring that boxes are placed and stacked gently, and properly secured from movement during transport. To lessen the exposure of the batteries to heat, metal shipping containers should be ventilated and kept away from heat sources such as ship's engines or direct sunlight. Stowage on ships must be below deck, while during other transport (road, rail, etc) and on/off loading, exposure to direct sunlight should be kept to a minimum.