

PATENT SPECIFICATION

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(54) ALKALINE ELECTRIC CELL

(71) We, KABUSHIKI KAISHA DAINI SEIKOSHA, a Japanese company of 31-1, 6-chome, Kameido, Koto-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to alkaline cells.
 10 In general, alkaline cells such as nickel-zinc cells, air-zinc cells, iron-nickel cells, alkali-manganese cells, mercury-oxide cells, silver oxide cells, divalent silver oxide cells etc. maintain their discharge voltage at a certain
 15 constant value substantially throughout their useful life.

According, it has been very difficult to determine when such conventional alkaline cells are approaching the end of their useful
 20 life. Thus, if a conventional alkaline cell is used in very important apparatus such as an artificial cardio-stimulating device, which has a direct effect upon human life, there is the serious disadvantage that the alkaline cell
 25 must be replaced after a predetermined time for safety even though it has not reached the end of its useful life.

The present invention seeks to provide an alkaline cell the approach of the end of whose
 30 useful life can be detected.

Anode active material comprising zinc and indium is known and is made by treating zinc particles with a solution consisting of indium or an indium compound dissolved in
 35 hydrochloric acid, and washed with a large

quantity of water. Anode active material comprising zinc, indium and mercury is known but to prevent mercury pollution, the mercury content is reduced by adding micro-quantities, e.g. 0.0001 - 2% by weight of indium based
 40 upon the combined weights of zinc, indium and mercury.

Further, anode active material consisting of a zinc alloy including 0.5% by weight of lead based upon the combined weights of lead and
 45 zinc, 0.02% by weight of cadmium based upon the combined weights of cadmium and zinc and 0.02% by weight of indium based upon the combined weights of indium and zinc is known.

Moreover, anode active material consisting
 50 solely of indium is known. For example, an indium-mercury oxide (In/HgO) alkaline cell (open circuit voltage $E_o \approx 1.16V$) and an indium-monovalent silver oxide (In/Ag₂O) cell (open circuit voltage $E_o \approx 1.35V$) have been
 55 produced in the past.

However, although indium is excellent as or as a constituent of anode active material as also is zinc, it is a very rare material as a natural resource and is highly priced with the result
 60 that alkaline cells incorporating indium have not been developed extensively.

According to one aspect of the present invention there is provided an alkaline cell including anode active material composed of
 65 zinc, indium and mercury, there being at least 2% by weight of indium based upon the combined weight of indium and zinc.

As mentioned above the indium content of conventional alkaline cells is small and is less
 70

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than 2% by weight for the purpose of decreasing the mercury content of the anode active material. The purpose of indium in an alkaline cell according to the present invention is different and is to produce, for example, an indium-mono silver oxide potential ($E_0 = 1.35V$) when the alkaline cell is approaching the end of its useful life, and to this end at least 2% by weight of indium based upon the combined weight of indium and zinc is incorporated in the anode active material. Since the main constituent of the anode active material is zinc, the cost of incorporating indium therein is not unduly high.

As an alkaline cell according to the present invention approaches the end of its useful life, this can be detected by the change in discharge voltage thereof and so the alkaline cell may be replaced before the instrumental equipment being driven thereby ceases to function altogether.

The anode active material may contain up to 10% by weight of indium based upon the combined weight of indium and zinc.

Preferably the anode active material contains at least 2% by weight of mercury based upon the combined weight of mercury and zinc.

The alkaline cell may contain up to 14% by weight of mercury based upon the combined weight of mercury and zinc.

The alkaline cell may have a depolarising mix comprising or including a monovalent silver oxide or divalent silver oxide.

The anode active material preferably includes a gelatiniser. The gelatiniser may be any one or more of sodium polyacrylate, carboxymethyl cellulose, polyvinyl alcohol, polyethylene glycol, soluble starch, sodium alginate and corn starch.

The zinc, indium and mercury may be in the form of an alloy. Alternatively the zinc and mercury are in the form of an alloy. In this instance the indium may be incorporated into the alloy in solid form. The indium may, thus, be in the form of balls or a sheet.

According to a further aspect of the present invention there is provided a silver oxide alkaline battery cell comprising a cathode active material consisting essentially of a mixture of monovalent silver oxide and graphite or a compound of which the main ingredient is divalent silver oxide, an alkaline electrolyte and an anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state and indium balls, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication

that the cell is nearing the end of its useful life.

According to another aspect of the present invention there is provided a button-type battery cell for an electric watch comprising a cup-shaped cathode container serving as the cathode terminal of said cell; cathode active material, a barrier and alkali electrolyte absorbent means contained in said cathode container, said cathode active material consisting essentially of a mixture of monovalent oxide and graphite or a compound of which the main ingredient is divalent silver oxide; an anode container serving as the anode terminal of said cell, anode active material contained in said anode container, said anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state, and indium balls in said anode container, and insulating gasket means sealing said cathode container and anode container together, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life.

According to a yet further aspect of the present invention, there is provided a button-type battery cell for an electric watch comprising a cup-shaped cathode container serving as the cathode terminal of said cell; cathode active material, a barrier and alkali electrolyte absorbent means contained in said cathode container, said cathode active material consisting essentially of a mixture of monovalent oxide and graphite or a compound of which the main ingredient is divalent silver oxide; an anode container serving as the anode terminal of said cell, anode active material contained in said anode container disposing a layer of indium on part or all of the inner surface, said anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state in said anode container, and insulating gasket means sealing said cathode container and anode container together, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life.

The invention is illustrated, merely by way

of example, in the accompanying drawings, in which:—

Figure 1 is a schematic cross-section of a known silver oxide cell;

5 Figure 2 shows graphically the relationship between the theoretical electric capacity of indium in anode active material in comparison with the overall theoretical anode electric capacity for change in indium content based upon the weight of zinc;

10 Figure 3 illustrates the discharge characteristics of an alkaline cell according to the present invention and a conventional alkaline cell;

15 Figure 4 illustrates the discharge characteristics of alkaline cells according to the present invention for different anode active materials containing various amounts of indium;

20 Figure 5 shows the self-discharging rates of alkaline cells according to the present invention with variation of indium contents, and conventional alkaline cells;

25 Figure 6 shows the self-discharging rates of alkaline cells according to the present invention with variation in mercury contents;

30 Figure 7 shows, in cross-section, part of one embodiment of an alkaline cell according to the present invention; and

35 Figure 8 shows, in cross-section, part of another embodiment of an alkaline cell according to the present invention.

Figure 1 illustrates a silver oxide cell of Japanese Industrial Standard GS-12 type (11.6 mm diameter x 4.2 mm high). A cathode container 1 houses a depolarising mix 2 composed either of monovalent silver oxide (Ag_2O) and graphite or acetylene black, or of mainly divalent silver oxide (AgO), a separator 3, a plastic ring 4, an electrolyte absorbing material 5, an anode cap 7 housing anode active material 6 and a gasket or grommet 8 made of a suitable polyamide resin for electrically insulating the anode cap from the cathode container, and sealing the alkaline cell against leakage.

The invention will be further described by way of the following examples.

EXAMPLE 1

50 Figure 2 shows the theoretical electric capacity of indium in an anode active material in comparison with the overall theoretical anode electric capacity with change in the indium content based upon the combined weight of indium and zinc, the mercury content being constant. It will be appreciated from Figure 2 that the useful life of an indium-monovalent silver oxide alkaline cell ($\text{In-Ag}_2\text{O}$)-discharge voltage 1.37 - 1.30V, external resistance $R = 7.5 \text{ K}\Omega$ can be set arbitrarily as desired by varying the indium content relative to the zinc content. A zinc-monovalent silver oxide alkaline cell ($\text{Zn-Ag}_2\text{O}$) has a discharge voltage of 1.59 - 1.40 V through an external resistance $R = 7.5 \text{ K}\Omega$.

2 parts by weight of indium and 10.9 parts by weight of mercury were placed in a suitable glass bottle and mixed by a light shaking action to produce a liquid indium-mercury alloy.

Subsequently 98 parts by weight of a zinc powder of 48 - 150 mesh were put into the bottle, the bottle sealed and then shaken for about 3 hours. Next, the bottle was heated for about one hour at a constant temperature of 60°C , and a diffusion and cross-linking reaction between the zinc, indium and mercury thoroughly completed. Then, after cooling, the resultant powder of indium-mercury-zinc alloy was screened with a 48 - 150 mesh screener and thereafter used as anode active material.

80 The indium-mercury-zinc alloy powder so produced was mixed with a gelatiniser, such as, for example, one or more of sodium polyacrylate, carboxymethyl cellulose, polyvinyl alcohol, polyethylene glycol, soluble starch, sodium alginate, and corn starch, and thereafter gelatinised with an alkaline electrolyte such as, for example, sodium hydroxide, potassium hydroxide and lithium hydroxide, or press-formed, so as to produce the anode active material.

An alkaline cell according to the present invention of the type illustrated in Figure 1 but using the above anode active material was produced. This alkaline cell was discharged through a constant resistance of $7.5 \text{ K}\Omega$ at room temperature, and the discharge curve A shown in Figure 3 was produced. A plateau *a-b* shows the zinc-monovalent silver oxide discharge potential and a plateau *c-d* shows the indium-monovalent silver oxide discharge potential. Curve B in Figure 3 is the discharge curve for a conventional alkaline cell under the same conditions as the alkaline cell according to the present invention.

105 In the same manner as that described above, anode active material containing 4%, 6%, 8%, 10% and 12% by weight of indium based upon the combined weight of indium and zinc, zinc was produced and alkaline cells of the type illustrated in Figure 1 were made using these anode active materials. Figure 4 shows the discharge characteristics of such alkaline cells, when discharged through a constant resistance of $7.5 \text{ K}\Omega$ at room temperature, Curves C, D, E, F, G, H showing the discharge characteristics for the alkaline cells having anode active materials containing 2%, 4%, 6%, 8%, 10% and 12% by weight of indium based upon the combined weight of indium and zinc, respectively.

115 As will be appreciated from Figure 4, the time duration of the indium-monovalent silver oxide potential increases as the indium content of the anode active material increases.

120 However, as the indium content increases, the zinc discharge capacity decreases since the total quantity of anode active material for the alkaline cell is constant. That is to say, the time duration of the zinc-monovalent silver 130

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oxide potential is reduced as the time duration of the indium-monovalent silver oxide potential increases and so the operating time of an electronic instrument driven by the alkaline cell is reduced. Thus, the upper limit of the indium content based upon the combined weight of indium and zinc is for most practical purposes 10% by weight. The minimum time duration for the indium-monovalent silver oxide potential to make detection of the approach of the end of the useful life of the alkaline cell possible by operating a suitable alarm device (not shown) is, in practical terms, achieved by 2% by weight of indium based upon the combined weight of indium and zinc in the anode active material.

EXAMPLE 2

4.8 parts by weight of indium (5% by weight based upon the combined weight of indium and zinc) and 8 parts by weight of mercury (8% by weight based upon the weight of mercury and zinc) are placed in a suitable glass bottle and mixed by a light shaking action to produce a liquid indium-mercury alloy. Subsequently 92 parts by weight of a zinc powder of 48 - 150 mesh were put into the bottle, the bottle sealed and shaken for about 3 hours. Next, the bottle was heated for about one hour at a constant temperature of 60°C and a diffusion and cross-linking reaction between the zinc, indium and mercury thoroughly completely. Then, after cooling, the resultant indium-mercury zinc alloy powder was screened with a 48 - 150 mesh screener and thereafter was used as anode active material. The indium-mercury-zinc alloy so produced was mixed with a gelatiniser, such as, for example, sodium polyacrylate and carboxymethyl cellulose and thereafter gelatinised with an alkaline electrolyte or press-formed so as to produce the anode active material.

An alkaline cell according to the present invention of the type illustrated in Figure 1 but using the above anode active material was produced and its self-discharging rate was investigated.

After keeping the alkaline cells according to the present invention and conventional alkaline cells at a constant temperature of 60°C for 10, 20, 30 and 40 days, the discharge capacities thereof were calculated by discharging them through a constant resistance of 7.5 KΩ at room temperature and measuring the primary discharge capacities.

The formula for the self-discharging rate is as follows:

$$\frac{Co - Ci}{Co} \times 100 (\%),$$

where, Co is the primary discharge capacity through a resistance of 7.5 KΩ measured at 25°C, and

Ci is the discharge capacity measured at 25°C through a resistance of 7.5 KΩ after keeping the cell at a constant temperature of 60°C for 10, 20, 30 and 40 days.

Figure 5 shows (Curve I) the self-discharging rates of the alkaline cells according to this Example compared with a conventional alkaline cell (Curve K) whose anode active material does not contain indium. These curves show the mean values of self discharging rates for batches each containing 25 cells. It will be seen from Figure 5 that the self discharging rates of both the alkaline cells of this Example and the conventional alkaline cells do not differ i.e. the indium content in the anode active material has no deleterious effect upon the self-discharging rate of the alkaline cells of this Example.

Therefore, the alkaline cell of this Example has a relatively low discharging rate and superior storage ability. It has been confirmed by experiment that 20 days storage at 60°C and 40 days storage at the same temperature are respectively equivalent to one year's storage at room temperature and two years storage at room temperature.

Accordingly, the self discharging rate of the alkaline cell of this Example after storing two years is estimated to be under 15% and this has not been found to cause any problems in use.

In the same manner anode active material in which the indium content based upon the combined weight of indium and zinc, has been fixed at 5% and the mercury content, based upon the combined weight of mercury and zinc, has been changed, has been used in alkaline cells according to this Example and their self-discharging rates have been investigated. Anode active material containing 2%, 4%, 6%, 8%, 10%, 12% and 14% by weight of mercury based on the combined weight of mercury and zinc have been produced and the alkaline cells of the type illustrated in Figure 1, but with these anode active materials, have been produced and the self discharging rates have been measured.

Figure 6 shows the self discharging rates of the alkaline cells of this Example referred to above measured after 20 days storage at 60°C. As will be clear from Figure 6, if the mercury content is within the range of 2 - 14% by weight based upon the combined weight of mercury and zinc, the self discharging rates thereof are trouble-free in practice. If the mercury content decreases below 2% by weight based upon the combined weight of mercury and zinc, the cell discharging rate increases and when the alkaline cell is excessively discharged, there is a danger of the alkaline cell swelling due to gas generation in the anode active material. On the other hand, if the mercury content increases beyond 14% by weight based upon the combined weight of mercury and zinc, since the quantity of the anode active material is limited, the discharge

capacity of the alkaline cell is reduced because of the reduction in the amount of zinc, in spite of decreasing the self discharging rate.

Thus, for practical purposes, the anode active material for an alkaline cell according to the present invention contains 2 - 10% by weight of indium based upon the combined weight of indium and zinc and 2 - 14% by weight of mercury based upon the combined weight of mercury and zinc.

EXAMPLE 3

95 parts by weight of zinc of 48 - 150 mesh and 10 parts by weight of indium (III) chloride (InCl_3) were mixed and stirred with 500 ml of distilled water in a glass container and, after the supernatant liquid thereof was removed, 7 parts by weight of mercury (II) chloride (HgCl_2) and 500 ml of distilled water were added and the mixture stirred. The supernatant liquid was again removed, and the resultant zinc-indium-mercury powder neutralized with sodium carbonate and washed with distilled water. Then, the powder was dried and screened through a 48 - 150 mesh screener. The resultant alloy powder contained, in weight ratio, Zn:In:Hg = 90:5:5.

This alloy powder was mixed with a gelatiniser such as, for example, sodium polyacrylate, carboxymethyl cellulose and polyvinyl alcohol and gelatinised with alkaline electrolyte or press-formed, to form anode active material.

An alkaline cell according to the present invention, of the type illustrated in Figure 1, but using this anode active material was discharged through a constant resistance of 7.5 K Ω at room temperature. The alkaline cell produced a voltage of 1.57 - 1.40 V for 500 - 550 hours and a voltage of 1.40 - 1.20V was 2 - 15 hours.

By measuring and detecting the voltage produced by the alkaline cell, the consumption of main anode active material, i.e. zinc, and the approach of the end of the useful life of the alkaline cell can thus be detected.

Accordingly, various electronic instruments, such as electronic wrist watches, cameras, table calculators, pocket bells and artificial cardio stimulating devices using the alkaline cell of this Example, can be designed to detect the approach of the end of the useful life of the alkaline cell before the instrument stops functioning altogether. To this end, such instruments may have a display mechanism operated by the change in discharge voltage of the alkaline cell to warn of the approach of the end of the useful life of the battery. For instance, the approach of the end of the useful life of the battery may be indicated by causing a warning lamp to flash, by energising a speaker or buzzer, by changing the movement of clock hands or the like, by changing the colour of the display produced by a liquid crystal display device or of luminous diodes. These are, however, only examples of how a warning of the approach of the end of the use-

ful life of the alkaline cell may be given.

An alkaline cell according to the present invention may be used as a secondary battery, it being charged by a solar cell or battery or other charging means when the alkaline cell is approaching the end of its useful life. Thus various electronic instruments may be designed to continue to operate even though the alkaline cell is approaching the end of its useful life and needs to be replaced.

The anode active material may, as in this Example, include zinc powder as an initial ingredient, but also can use zinc plate, zinc block, zinc foil or fibroid zinc, as an initial ingredient, as well as other soluble indium compounds apart from indium chloride.

EXAMPLE 4

95 parts by weight of zinc powder of 48 - 150 mesh and 5 parts by weight of indium were placed in a glass container containing 500 ml of 85% diluted hydrochloric acid, and then were mixed and stirred until a zinc-indium alloy was produced. Thereafter, 5 parts by weight of mercury was added and the contents of the glass container mixed and stirred again until a zinc-indium-mercury alloy was produced. After removing the solution from the container, this zinc-indium-mercury alloy was washed with distilled water and dried, and screened through a 48 - 150 mesh screener to be used as anode active material of an alkaline cell according to the present invention.

Zinc powder is used in this Example but other forms of zinc can also be used. Furthermore, in this Example, mercury is added after producing the zinc-indium alloy but the mixing sequence of the zinc, indium and mercury can be changed in many ways. For instance, the zinc may be added after producing an indium-mercury alloy and also the three constituents may be mixed together at the same time. Moreover, the acid used as a reacting agent in Examples 3 and 4 may be replaced by, for example, an alkaline solution such as sodium hydroxide, or a mixture of ammonium hydroxide and ammonium chloride.

EXAMPLE 5

A zinc-indium-mercury alloy was made by amalgamating with mercury or a mercury compound a zinc-indium alloy produced by a melting and casting process. The zinc-indium-mercury alloy was then used as anode active material in an alkaline cell according to the present invention, the zinc-indium-mercury alloy containing at least 2% by weight of indium based upon the combined weight of indium and zinc.

EXAMPLE 6

Figure 7 is a portion of an alkaline cell according to the present invention. Anode active material 16 is disposed within an anode cap 17 forming a negative terminal. The anode active material includes an anode mix 19 of amalgamated zinc powder of 48 - 150 mesh containing 5% by weight of mercury based upon the combined weight of mercury and zinc

either with a gelatiniser such as sodium polyacrylate or carbonylmethyl cellulose, or press-formed, and indium balls 20 2 - 10 microns in size.

5 In this Example indium balls are used but the shape of the indium, which is in solid form, can be selected as desired. For instance, indium in the nature of foil, plate, thready type, fibroid type or block may be used. The amount of indium based upon the combined amount of indium and zinc is at least 2% by weight.

The electrical connection between the indium balls and the anode cap 17, if required, may be achieved by, for example, electric welding, pressure fastening, heat fusion fastening etc.

EXAMPLE 7

Figure 8 illustrates a portion of another alkaline cell according to the present invention. 20 Anode active material 26 consists of an anode mix 29 of a zinc amalgam formed from zinc powder of 48 - 150 mesh either with a gelatiniser such as sodium polyacrylate or carboxymethyl cellulose, or press-formed, and a layer 25 31 of indium disposed on part or all of the inner surface of the anode cap 27.

The indium layer 31 may be formed by ion plating, electroplating, vacuum evaporating coating or sputtering processes. Alternatively, 30 the indium sheet and the plate material of the anode cap may be formed by cladding prior to formation of the latter. The amount of indium is at least 2% by weight based upon the combined weight of indium and zinc.

35 The discharge characteristics of the alkaline cells of Figures 7 and 8 have two plateaus similar to the alkaline cells of Examples 1 to 3. Accordingly, the consumption of the zinc, which is the main active material, as the alkaline cell discharges can be detected and the approach of the end of the useful life of the alkaline cell determined.

The above Examples relate to silver oxide cells ($\text{Zn-Ag}_2\text{O}$, Zn-AgO) but the present invention can be applied to other alkaline cells such as nickel-zinc cells, air-zinc cells, alkalimanganese cells, mercury-oxide cells etc.

An alkaline cell according to the present invention may be used in various instruments, 50 the approach of the end of the useful life of the alkaline cell being detectable before the instrument ceases to operate altogether. Thus an alkaline cell according to the present invention may be used to advantage as a power source in, for example, electronic wrist watches, cameras, pocket bells, artificial 55 cardio-stimulating devices, table calculators, cigarette lighters, hearing aids, etc. and generally has a great industrial application.

60 Having regard to the provisions of Section 8 of the Patents Act, 1949, we direct attention to our Patent No. 1 507 120.

We hereby disclaim the matter claimed in the specification of Patent No. 1 507 120, and 65 subject to the foregoing disclaimer.

WHAT WE CLAIM IS:

1. An alkaline cell including anode active material composed of zinc, indium and mercury, there being at least 2% by weight of indium based upon the combined weight of indium and zinc. 70

2. An alkaline cell as claimed in claim 1 in which the anode active material contains up to 10% by weight of indium based upon the combined weight of indium and zinc. 75

3. An alkaline cell as claimed in claim 1 or 2 in which the anode active material contains at least 2% by weight of mercury based upon the combined weight of mercury and zinc.

4. An alkaline cell as claimed in any preceding claim in which the anode active material contains up to 14% by weight of mercury based upon the combined weight of mercury and zinc. 80

5. An alkaline cell as claimed in any preceding claim having a depolarising mix comprising or including a monovalent silver oxide or divalent silver oxide. 85

6. An alkaline cell as claimed in any preceding claim in which the anode active material includes a gelatiniser. 90

7. An alkaline cell as claimed in claim 6 in which the gelatiniser is any one or more of sodium polyacrylate, carboxymethyl cellulose, polyvinyl alcohol, polyethylene glycol, soluble starch, sodium alginate and corn starch. 95

8. An alkaline cell as claimed in any preceding claim in which the zinc, indium and mercury are in the form of an alloy.

9. An alkaline cell as claimed in any of claims 1 to 7 in which the zinc and mercury are in the form of an alloy. 100

10. An alkaline cell as claimed in claim 9 in which the indium is incorporated into the alloy in solid form. 105

11. An alkaline cell as claimed in claim 10 in which the indium is in the form of balls or a sheet.

12. A silver oxide alkaline battery cell comprising a cathode active material consisting essentially of a mixture of monovalent silver oxide and graphite or a compound of which the main ingredient is divalent silver oxide, an alkaline electrolyte and an anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state and indium balls, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life. 125

13. A button-type battery cell for an electric watch comprising a cup-shaped cathode 130



either with a gelatiniser such as sodium polyacrylate or carbonylmethyl cellulose, or press-formed, and indium balls 20 2 - 10 microns in size.

- 5 In this Example indium balls are used but the shape of the indium, which is in solid form, can be selected as desired. For instance, indium in the nature of foil, plate, thready type, fibroid type or block may be used. The amount of indium based upon the combined amount of
- 10 indium and zinc is at least 2% by weight.

The electrical connection between the indium balls and the anode cap 17, if required, may be achieved by, for example, electric welding, pressure fastening, heat fusion fastening etc.

EXAMPLE 7

Figure 8 illustrates a portion of another alkaline cell according to the present invention.

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- 25 31 of indium disposed on part or all of the inner surface of the anode cap 27.

The indium layer 31 may be formed by ion plating, electroplating, vacuum evaporating coating or sputtering processes. Alternatively,

30 the indium sheet and the plate material of the anode cap may be formed by cladding prior to formation of the latter. The amount of indium is at least 2% by weight based upon the combined weight of indium and zinc.

- 35 The discharge characteristics of the alkaline cells of Figures 7 and 8 have two plateaus similar to the alkaline cells of Examples 1 to 3. Accordingly, the consumption of the zinc, which is the main active material, as the alkaline cell discharges can be detected and the
- 40 approach of the end of the useful life of the alkaline cell determined.

The above Examples relate to silver oxide cells ($\text{Zn-Ag}_2\text{O}$, Zn-AgO) but the present invention can be applied to other alkaline cells such as nickel-zinc cells, air-zinc cells, alkalimanganese cells, mercury-oxide cells etc.

- An alkaline cell according to the present invention may be used in various instruments, the approach of the end of the useful life of the alkaline cell being detectable before the instrument ceases to operate altogether. Thus an alkaline cell according to the present invention may be used to advantage as a power
- 50 source in, for example, electronic wrist watches, cameras, pocket bells, artificial cardio-stimulating devices, table calculators, cigarette lighters, hearing aids, etc. and generally has a great industrial application.

60 Having regard to the provisions of Section 8 of the Patents Act, 1949, we direct attention to our Patent No. 1 507 120.

We hereby disclaim the matter claimed in the specification of Patent No. 1 507 120, and

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WHAT WE CLAIM IS:

1. An alkaline cell including anode active material composed of zinc, indium and mercury, there being at least 2% by weight of indium based upon the combined weight of indium and zinc. 70

2. An alkaline cell as claimed in claim 1 in which the anode active material contains up to 10% by weight of indium based upon the combined weight of indium and zinc. 75

3. An alkaline cell as claimed in claim 1 or 2 in which the anode active material contains at least 2% by weight of mercury based upon the combined weight of mercury and zinc.

4. An alkaline cell as claimed in any preceding claim in which the anode active material contains up to 14% by weight of mercury based upon the combined weight of mercury and zinc. 80

5. An alkaline cell as claimed in any preceding claim having a depolarising mix comprising or including a monovalent silver oxide or divalent silver oxide. 85

6. An alkaline cell as claimed in any preceding claim in which the anode active material includes a gelatiniser. 90

7. An alkaline cell as claimed in claim 6 in which the gelatiniser is any one or more of sodium polyacrylate, carbonylmethyl cellulose, polyvinyl alcohol, polyethylene glycol, soluble starch, sodium alginate and corn starch. 95

8. An alkaline cell as claimed in any preceding claim in which the zinc, indium and mercury are in the form of an alloy.

9. An alkaline cell as claimed in any of claims 1 to 7 in which the zinc and mercury are in the form of an alloy. 100

10. An alkaline cell as claimed in claim 9 in which the indium is incorporated into the alloy in solid form. 105

11. An alkaline cell as claimed in claim 10 in which the indium is in the form of balls or a sheet.

12. A silver oxide alkaline battery cell comprising a cathode active material consisting essentially of a mixture of monovalent silver oxide and graphite or a compound of which the main ingredient is divalent silver oxide, an alkaline electrolyte and an anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state and indium balls, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life. 115 120 125

13. A button-type battery cell for an electric watch comprising a cup-shaped cathode 130



container serving as the cathode terminal of said cell; cathode active material, a barrier and alkali electrolyte absorbent means contained in said cathode container, said cathode active material consisting essentially of a mixture of monovalent oxide and graphite or a compound of which the main ingredient is divalent silver oxide; an anode container serving as the anode terminal of said cell, anode active material contained in said anode container, said anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state, and indium balls in said anode container, and insulating gasket means sealing said cathode container and anode container together, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life.

14. A cell as claimed in claim 12 or 13, in which said indium balls are 2-10 micron in size.

15. A cell as claimed in claim 12 or 13 in which the shape of indium is selected from foil, plate, thready type, fibroid type or block.

16. A cell as claimed in any of claims 12 to 15 in which the electrical connection between the indium and the anode cap is achieved by electric welding, pressure fastening, heat fusion fastening.

17. A cell as claimed in any of claims 12 to 16 in which said powdered amalgamated zinc is 48-150 mesh.

18. A cell as claimed in any of claims 12 to 17 in which the proportion of indium to zinc is 2-10%.

19. A cell as claimed in any of claims 12 to 18 in which the proportion of mercury to zinc is 2-14%.

20. A cell as claimed in any of claims 12 to 19 in which said binder is selected from the group consisting of carboxy methyl cellulose or sodium polyacrylate.

21. A button-type battery cell for an electric watch comprising a cup-shaped cathode container serving as the cathode terminal of said cell; cathode active material, a barrier and alkali electrolyte absorbent means contained in said cathode container, said cathode active material consisting essentially of a mixture of monovalent oxide and graphite or a compound

of which the main ingredient is divalent silver oxide; an anode container serving as the anode terminal of said cell, anode material contained in said anode container disposing a layer of indium on part or all of the inner surface, said anode active material consisting essentially of powdered amalgamated zinc uniformly mixed with a binder and pressed into formed or gelled state in said anode container, and insulating gasket means sealing said cathode container and anode container together, said cell having a first substantially constant predetermined discharge voltage until the zinc of said anode active material is substantially used up and thereafter having a second substantially constant predetermined discharge voltage which is lower than said first voltage, for a predetermined period of time, whereby the drop in voltage from said first voltage to said second voltage provides an advance indication that the cell is nearing the end of its useful life.

22. A cell as claimed in claim 21 in which the indium layer is a layer formed by ionplating, electroplating, vacuum evaporating coating or sputtering processes.

23. A cell as claimed in claim 21 or 22 in which the anode container is a container formed by cladding the indium sheet and the plate material of the anode cap prior to formation of the latter.

24. A cell as claimed in any of claims 21 to 23 in which said powdered amalgamated zinc is 48 - 150 mesh.

25. A cell as claimed in any of claims 21 to 24 in which the proportion of indium to zinc is 2 - 10%.

26. A cell as claimed in any of claims 21 to 25 in which the portion of mercury to zinc is 2 - 14%.

27. A cell as claimed in any of claims 21 to 26 in which said binder is selected from the group consisting of carboxymethylcellulose or sodiumpolyacrylate.

28. An alkaline cell as claimed in any preceding claim in which the anode active material is as described in any of Examples 1 to 8.

29. An alkaline cell as substantially as herein described with reference to and as shown in any of Figures 2 to 8 in the accompanying drawings.

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