

DRY CELL BATTERIES  
CHEMISTRY AND DESIGN

**DRY CELL BATTERIES**  
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**NOYES DATA CORPORATION**

**Park Ridge, New Jersey**

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## FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1969 relating to the chemistry and design of dry cell batteries.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, commercially oriented review of dry cell chemistry and technology.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. One should have to go no further than this condensed information to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Specialized techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, printing, binding and shipping methods can render a technical or scientific book quite obsolete before the potential user gets to see it.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

## 15 Reasons Why the U.S. Patent Office Literature Is Important to You—

- (1) The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
- (2) The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
- (3) The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
- (4) An important feature of the patent literature is that it can serve to avoid duplication of research and development.
- (5) Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
- (6) It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
- (7) Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
- (8) Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
- (9) Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
- (10) Obtain licenses — many U.S. chemical patents have not been developed commercially.
- (11) Patents provide an excellent starting point for the next investigator.
- (12) Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
- (13) Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
- (14) Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
- (15) It is a creative source of ideas for those with imagination.

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## INTRODUCTION

Of the several billion batteries manufactured throughout the world each year, the conventional dry cell ( $\text{Zn-MnO}_2$ , Leclanché) still accounts for well over 70% of the market. This cell, first described by George Leclanché in 1868, evolved into the "dry cell" by immobilizing the electrolyte on a porous material and was mass produced beginning in 1890. The alkaline dry cell, known in the early 1900's did not reach commercial production until 1949 due to need for better sealing techniques for the strong alkaline electrolytes. Indeed, much of the very recent battery design literature is devoted to sealing techniques which are adaptable to modern manufacturing methods.

Magnesium dry cell batteries have demonstrated almost double the capacity of the conventional zinc dry cell batteries at moderate discharge rates and have significantly increased the storage capability of such batteries. These batteries commonly employ either magnesium perchlorate or magnesium bromide as the electrolyte. Magnesium dry batteries are finding increasing use in military communication equipment and the cost of the batteries has dropped significantly over the past few years.

Alkaline zinc-mercury oxide cells were developed during World War II. By 1945, approximately one million cells were being produced each day. These cells, while expensive, do provide a relatively constant voltage during discharge and exhibit a good energy-to-volume ratio.

Alkaline silver oxide-zinc batteries are used in many military applications such as guided missiles, portable radios and radar equipment. Either the divalent silver oxide or monovalent silver oxide may be used as the cathode. These batteries exhibit high capacity per unit of weight, coupled with excellent high rate capabilities. Cells containing organic electrolytes are able to use high energy light metal electrodes such as lithium, which are incompatible with aqueous electrolytes. Typically, a lithium-cupric chloride cell in a propylene carbonate electrolyte will provide high operating voltages and energy densities.

In recent years, much research effort has been devoted to solid state devices employing solid electrolytes. Various metal-halogen compounds and charge transfer

complexes have been developed as electrolytes and for use in electrodes. These solid electrolyte batteries are of considerable interest because of their exceptional stability, physical ruggedness, and ease of miniaturization. The efficiency of these cells is determined by the solid electrolyte which serves as an ionic conductor, and most of the recent effort has been directed to enhancing this ionic conductivity while minimizing cost.

The heat activated batteries (fused salt electrolyte) work on the principle that fused salts are ionically conductive and thus perform as an electrolyte. Much of the work on thermal batteries has been conducted for the military and little has been published to date.

The accelerating pace of technology in battery electrochemistry and design is nowhere more evident than in the patent literature. This book describes over 130 processes relating to recent developments in dry cell batteries employing zinc, magnesium, cadmium-nickel, lithium, solid state devices, organic electrolytes, and thermal activation. It includes many modern manufacturing techniques.

## BASIC ZINC DRY CELLS

### ELECTRODES

#### Wet Amalgamation Bonding

R.E. Ralston and Y.L. Ko; U.S. Patent 3,669,754; June 13, 1972; assigned to P.R. Mallory & Co. describe a negative electrode which is fabricated by a process which might be called "wet amalgamation bonding". A mixture of the following composition has been used to prepare electrodes of 65% porosity:

46.6 grams zinc  
6.0 grams mercurous chloride  
5.0 grams ammonium chloride  
1 drop glycerine

In mixing, one drop of glycerine is added to the proper weight of zinc particles of -100, +200 mesh, and mixed thoroughly to wet and cover the surfaces of the zinc particles. Mercurous chloride is added, again with complete mixing, to coat the surface of the zinc with amalgamating material. Ammonium chloride is then added and dispersed evenly. The mix is then ready for use.

The molded electrode is made by amalgamation-bonding zinc particles to a conductor of brass, or zinc plated brass, or amalgamated zinc plated brass. Preamalgamation not only cleans the surface but also decreases the tendency of the zinc plate on the conductor to be stripped off or go into solution in the ammonium chloride solution. This is accomplished by placing the conductor in a mold conveniently made of plastic, and applying the correct amount of electrode mix in contact with the surface to be bonded. Excess air is expelled and good particle-to-particle relationship established by vibration compacting.

While still confined in the mold, a quantity of saturated ammonium chloride solution is added to wet the electrode material and to initiate the reaction process. After approximately 15 minutes the electrode can be removed from the mold and placed in a solution of ammonium chloride, for 12 hours or more, to allow the bonding reaction

to reach completion; and then the electrode is washed and dried. The bonding action by this technique might be called solution sintering by liquid mercury. The initial reaction is the chemical displacement of zinc by mercury, depositing liquid mercury over the entire zinc surface. Immediately the mercury begins to alloy with the clean zinc, since the ammonium chloride acts as a flux to clean the zinc surface of oxide, and other unwanted matter, and the surface changes from 100% mercury to about 10% mercury as the homogeneous alloy forms.

However, during the early stages of the alloy formation, zinc dissolves in the liquid mercury which is concentrated at the points or areas of contact between particles, and forms a solid solution bond at these contact points or areas when the alloy formation is complete. The same type of bonding is also accomplished at the surface of the anode collector. The superiority of the molded anode has been demonstrated by the performance of alkaline manganese cells at minus 40°C. The following service was obtained with "C" cells on an intermittent duty cycle of 4 minutes on load per hour, 10 hours per day, 5 days per week to an end voltage of 0.93 volts on a 7.5 ohm load:

	<u>Minutes</u>
Conventional Brand A	3
Conventional Brand B	11
This process Molded Anode	190-200

#### Leached Amalgamated Zinc

R.R. Clune and H. Field; U.S. Patent 3,427,204; February 11, 1969; assigned to P.R. Mallory & Co., Inc. describe a battery system in which the efficiency is greatly enhanced, especially for low temperature usage. This increase in efficiency is among other features due to the presence, in the battery, of an anode consisting of porous zinc amalgam and utilizing ammonium chloride, mercurous chloride and magnesium sulfate. The anode is formed as a uniform, porous pellet by means primarily of reactive cementation of the mixed materials.

The extent of the anodic surface is greatly enhanced by the high porosity of the structure thus formed. After the chemical displacement reaction and cementation, excess unused materials are carefully leached away resulting in a highly porous and uniformly dense amalgamated zinc pellet of great surface area. The anode, moreover, is of much greater porosity and more consistent surface area, affording better electrolytic conductivity and lower impedance, and has a greater ability to hold more electrolyte than anodes priorly available. The preferred pelleted mixture consists primarily of about 55.4% zinc, 37.7% ammonium chloride, 6.9% mercurous chloride, and the rest an aliphatic solvent. The final anode structure has a porosity of about 77%, and consists essentially of about 90% zinc and 10% mercury.

This process enables alkaline cells to function at low temperatures (-30°C.) with up to 85% of their efficiency at normal temperatures. It is an improvement over common pellet, dispersed pellet or wound anode structures, which deliver at best 20% of room temperature performance at -30°C. and over such devices as heaters, frangible vials, antifreezes, etc., employed to obtain low temperature operation. These have added greatly to the complexity of the structure, while decreasing space available for active elements; e.g., depolarizer, anode and electrolyte.

The leached amalgamated anode of great porosity is produced as follows:

**Fabrication and Reactive Cementation** — Place 300 grams of ammonium chloride and 25 grams of magnesium sulfate into a blender. Introduce 916 grams of zinc and mix. Introduce 0.080 gram (approximately 50 drops) of a nonpolar, low volatility substance such as deodorized kerosene. Mix until uniform. The kerosene acts as a coating which prevents premature reaction of the material and as a blending agent to coat the pellets and cohere them in order to prevent stratification and segregation. This step assures uniform blending so that homogeneity is obtained in the mix.

Introduce 236 grams of mercurous chloride and mix until uniform. It is required that all mixing be done at a temperature of 65°F. maximum and at a relative humidity of 40% maximum. The mix is then pelletized at a pressure of about 12,800 pounds per square inch.

**Leaching** — The pellets are placed in washing trays and are then immersed in a saturated solution of ammonium chloride. The pellets must be soaked for a minimum of 1/2 hour in the saturated solution of ammonium chloride. The pellets are then leached until free of chloride ion. Test to determine an absence of chloride ion by the use of silver nitrate added to the water drippings from the washed pellets.

**Drying** — After leaching is completed by showing that all chloride ion is absent from the leaching water, place the anodes in a solution of methanol for about 10 minutes. The methanol is used to dry the anodes. Remove the pellets from methanol and place them in a vacuum oven preheated at 100°F. until the pellets are completely dried. The pellets are then stored in a dry atmosphere in a container which is air tight and which may include a desiccant.

#### Potassium Hydroxide Impregnation

R.W. Blossom and A. Charkey; U.S. Patent 3,655,451; April 11, 1972; assigned to Yardney International Corp. describe a process for manufacturing an electrode impregnated with potassium hydroxide. Potassium hydroxide in powder form having a low content of water is mixed with the anode metal in powder form and blended to form a coherent mixture. The mixture is spread over a conductive grid, subjected to a pressing operation to form a unitary structure of the desired electrode shape and then heated in the absence of air. The electrode is then stored in an airtight container. A strong KOH-impregnated metal anode capable of long storage is obtained.

In the manufacture of primary cells where quick activation is needed, several methods have been proposed for impregnating a zinc electrode with a potassium hydroxide electrolyte by immersing the completely formed zinc electrode in an alkaline solution. Thereafter, it is dried and placed in either cold storage or some closed environment devoid of water vapor to obtain a long-lasting electrode. However, it has been found that, during manufacture, these electrodes tend to be pyrophoric and will spontaneously burst into flame.

An alternate method for manufacturing such electrodes has been described where potassium hydroxide, in powder form is mixed with zinc, in powder form, spread over a conductive grid and subjected to a pressing operation to form the desired electrode shape. This method avoided the pyrophoric stage and provided usable electrodes.

The potassium hydroxide powder useful in the process may be purchased on the open market and should contain a very low amount of water. A preferable range is between 5 and 7% of  $H_2O$  by weight. It has been found that moisture contents of less than 3.5% should be avoided. Such substantially anhydrous KOH tends to cause caking and is difficult to repulverize. On the other hand, KOH powders with water contents of 10% or greater render the zinc/KOH mixture too pyrophoric. When handling this potassium hydroxide powder and the zinc/KOH mixture, safety precaution such as safety glasses and dust masks are recommended. Since KOH is very hygroscopic, it should be carefully stored to maintain the moisture range within the limits of 3.5 to 10% by weight.

In the preparation of the electrode, KOH in powder form is mixed with zinc in powder form. The ratio of KOH to zinc powder may be from 0.15 to 0.25 grams of KOH for each gram of zinc powder and preferably is above 0.23 gram. The zinc and KOH powders are well blended either by handmixing, by tumbling the powders or by large-scale blending equipment. The amount of KOH mixed with the zinc powder depends to some extent upon the desired concentration of the electrolyte after the addition of water in a battery system. In a battery of given configuration, the space available for the electrolyte also influences the amount of KOH. Too little KOH will prevent proper functioning of the electrolyte.

On the other hand, too much admixed KOH tends to render the electrode too brittle and of course reduces the amount of zinc available in the anode. A compromise must then be reached, keeping in mind these considerations. The amount of dry KOH added to the plate is such that the final concentration of electrolyte in the assembled cell of any configuration will be between 20 and 45% aqueous KOH. This means that the ratio of 0.015 to 0.25 grams of KOH per gram of zinc set forth above is useful for zinc-air cell having limited quantity of free electrolyte, e.g., a cell having 32 cc of electrolyte volume with 29.5 cc of zinc-electrode volume. In other configurations suitable adjustments are required.

The electrodes are fabricated by cold-pressing the composite Zn/KOH mixture on a supporting grid at various pressures. The grid may be made of expanded-metal meshes of copper, silver, or cold-rolled steel having 40 to 60% open area and 5 to 10 mil thickness. The mixture is evenly distributed into the grid and the composite is compressed at a pressure ranging, in a typical situation, from 4 to 10 tons per square inch. The preferable range is about 4.4 to 5.0 tons per square inch.

The final density of the pressed electrode is approximately 2.2 grams per cc. Since this compacted mass includes KOH, the addition of water which will dissolve the KOH renders the density of the zinc plate in the activated cell substantially lower. Thus, the zinc density is computed to provide the optimum of 1.8 grams per cc in situ. KOH impregnated zinc plates having thicknesses from 0.020 to 0.0200 inches have been made for the above described cells having a 32 cc electrolyte volume.

After compression, the dry plates are placed in an oven provided with a nonoxidizing atmosphere such as vacuum, nitrogen, hydrogen or argon, and are heated at temperatures in the range of 200° to 400°F., for a period of time sufficient to agglomerate the particles and bind them together with the water contained in the KOH powder acting as a binder. At the higher temperature, 10 minutes is sufficient to develop the strength of the electrode. At lower temperatures correspondingly longer times are necessary, but below 200°F. either the reaction of the interstitial water is not

started or the time required is too long for practical purposes, (in excess of 1 1/2 hours). Following the heating treatment, the plates are sealed in moistureproof composite bags made from craft paper, aluminum or polyethylene depending upon the desired storage time between electrode manufacture and complete battery fabrication or electrode insertion. It has been found that electrodes prepared from such Zn/KOH powder mixtures can be left exposed in air from 1 to 2 hours depending on the relative humidity. As a practical matter, however, pyrophoric conditions may arise when the KOH absorbs in excess of 10% of water.

Since oxidation of the plates is initiated after they have been exposed for more than the stated periods, and proceeds rapidly until the electrodes may ignite, sealing of the electrode must be completed before the specified time. The exact correlation between the rate of moisture pick-up leading to pyrophoric electrode oxidation and the relative ambient humidity has not been established. However, it has been observed that on days when the humidity is less than 40%, the plates can be exposed for about 2 hours. On days when the humidity is high, for instance greater than 60%, the plates should not be exposed to the air for more than 1 hour. Plate oxidation is best minimized by drying the atmosphere in the locale where the mixing, pressing, heat-treating and sealing operations are conducted.

The performance of the above described composite electrodes was evaluated with good results. In a typical example, the electrode for a cell was made by blending 30 grams of zinc powder with 7.4 grams of KOH powder, mold-pressing to a density of approximately 2.2 grams per cc and a thickness of 0.2 inches and subsequently heating at 300°F. for 20 minutes in a nitrogen-flushed oven. Sample electrodes were compared with electrodes prepared according to a previous process. It was found that the heat-treated electrodes of this process had much greater tensile strength, compressive strength and resistance to flexure.

In addition, when subjected to vibration tests, the electrodes survived frequencies and amplitudes that destroyed the referenced samples. The electrodes were then inserted into 12 mils pella separator bags and placed in an air cell having a 12-square inch cathode area. The cell was activated with 14 cc of distilled water and discharged immediately at rates of 2.5 amp. and 5.0 amp. At these discharges the respective plateau voltages were 1.06 and 1.02 volts, yielding further respective storage capacities of 13.7 and 12.9 amp. hours. The zinc utilization was respectively 2.33 and 2.45 grams per amp. hour. Statistically these performance data were identical with the unheated electrodes of the prior disclosure referred to.

#### Sintered Zinc Powder

In a process described by R.D. Weller; U.S. Patent 3,663,297; May 16, 1972; assigned to the U.S. Secretary of the Navy sintered zinc powder battery electrodes are prepared by (1) rinsing zinc powder with a solvent that dissolves zinc oxide at a faster rate than it dissolves zinc and which is saturated with a water-soluble salt having a higher melting point than zinc; (2) pouring off the solvent; (3) mixing the zinc with the water-soluble salt used in step (1); (4) packing the mixture around a metal screen that is made of a metal which is an electrical conductor having a higher melting point than zinc; (5) heating the packed article at a temperature above 419°C. but below the melting point of the water-soluble salt and the metal screen; (6) cooling the article; and (7) soaking the article in water to remove the water-soluble salt.

Example: 20 grams of zinc powder was rinsed with 1 N HCl which was saturated with NaCl. Contacting was maintained for about 30 seconds in order to remove the zinc oxide coating from the zinc particles. Most of the HCl was then poured off leaving the zinc powder damp. 8 grams of NaCl powder was added to the wet zinc making a damp mixture of NaCl and zinc powders. This mixture was packed into a die while it was still damp and pressed to 7,000 psi into an electrode which was approximately  $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{1}{8}$  inches. A silver metal screen was included in the middle for a current collector.

The pressed electrode, still damp, was held between two discs of sintered glass and placed into an argon atmosphere furnace which was heated up to 500°C. in approximately 15 minutes. This temperature was then held for about 1 more minute. After cooling the electrode was removed and soaked in water to dissolve the NaCl thus leaving the zinc electrode.

#### Addition of Stainless Steel Filaments to Cathode

C.K. Ching, W. Cohen and S. Tseng; U.S. Patent 3,660,167; May 2, 1972 describe an alkaline dry cell of high energy density in which a cathode of powdered manganese dioxide, carbon, and graphite has dispersed throughout it, short filaments of stainless steel, long filaments of stainless steel, and stainless steel powder.

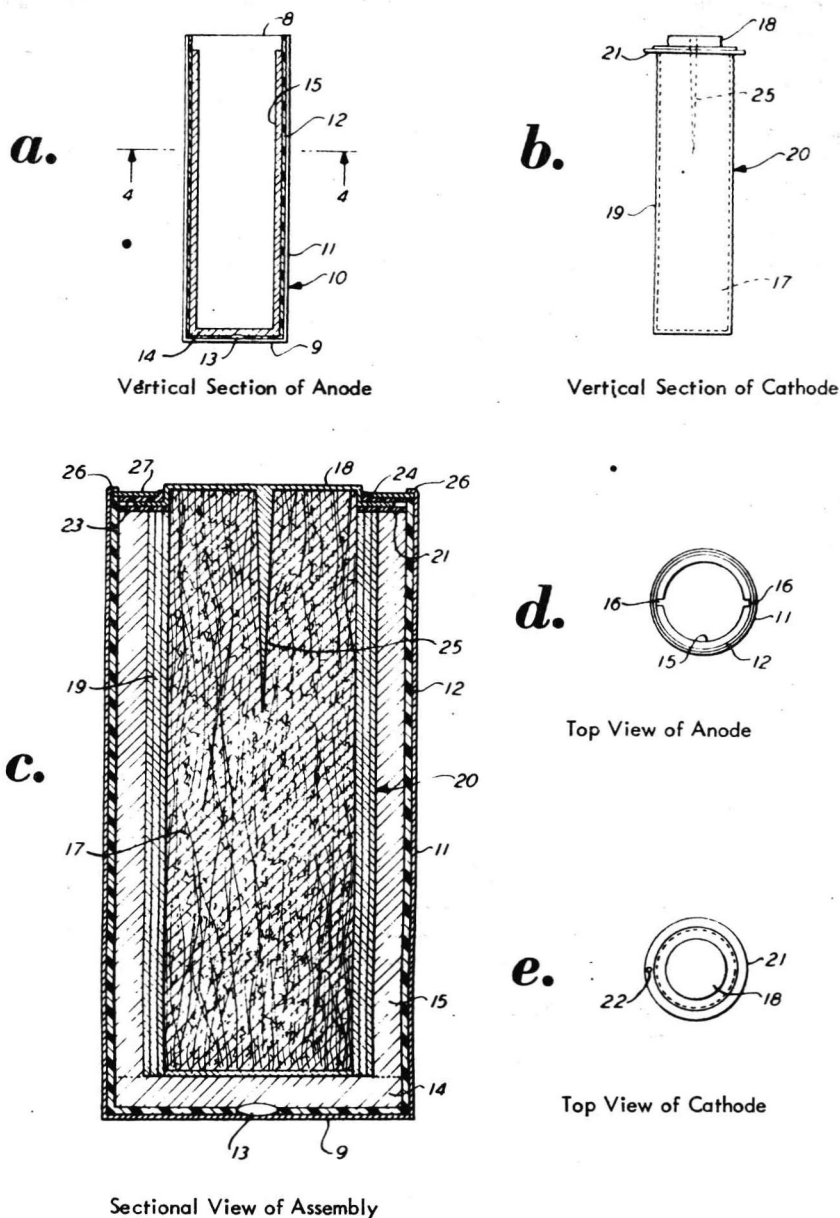
Referring to Figure 1.1, the anode (10) has a steel jacket (11) which is generally tubular with a closed bottom (9) and an open top (8). The jacket (11) is a protective shell or covering that protects the internal parts of the alkaline dry cell from impact damage or damage due to deformation of the cell. The steel jacket is approximately 0.010 inch thick. A preformed liner (12) of nonconductive material having an external diameter substantially equal to the internal diameter of the steel jacket (11) is inserted into the jacket (11) to cover the side wall and the bottom. It is preferred that the liner (12) be made of some plastic material such as polyethylene or polyvinyl chloride 0.006 inch thick. The liner (12) has a bottom center opening to which a contact button (13) is inserted.

Since the liner (12) is of dielectric material the contact button (13) establishes conductivity between the exterior of the liner (12) and the interior. A deposit of amalgamated zinc powder is now placed in the liner (12) to form the bottom (14) of the anode. The bottom (14) of the anode is a layer originally 0.150 inch thick. The thickness is not critical. The bottom (14) is in electrical conductive contact with the contact button (13) and in turn with the jacket (11). The contact (13) is preferably a stainless steel button formed of the 400 series. To complete the anode from the bottom (13) to the top, an expandable split mold is positioned in the liner (12), seated on the bottom (14).

The split mold has an external diameter of 0.437 inch leaving an interstitial space. The interstitial space is filled with amalgamated zinc powder to within approximately  $\frac{1}{16}$  of an inch from the top. A tapered pin is then inserted in the split mold. This expands the mold and compresses the amalgamated zinc powder to a thickness of approximately 0.030 inch. The tapered pin is removed and the split mold is thereupon withdrawn leaving a central cavity in the anode (15) for the insertion of a cathode assembly. Two generally vertical slots are formed in the vertical wall of the anode (15) by reason of the expansion of the split mold.



FIGURE 1.1: ADDITION OF STAINLESS STEEL FILAMENTS TO CATHODE



Source: C. K. Ching, W. Cohen and S. Tseng; U.S. Patent 3,660,167; May 2, 1972.