July 27, 1937. O. E. RUHOFF ET AL 2,088,307

DRY CELL, CORE THEREFOR AND METHOD OF PRODUCING SAME

Filed Dec. 8, 1934

Fig. 1

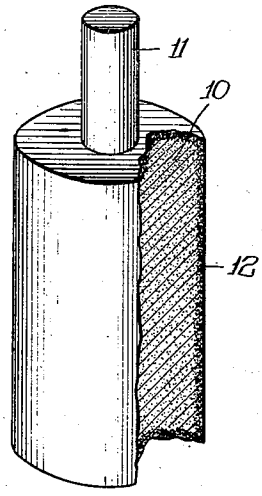


Fig. 2

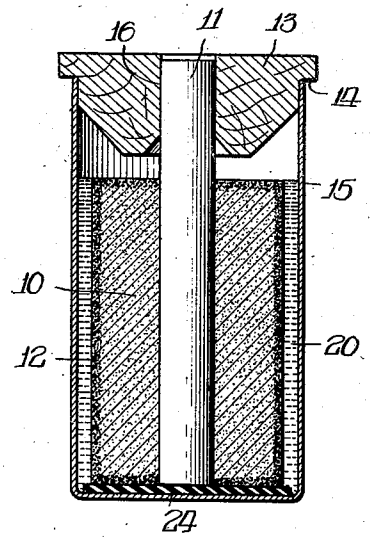


Fig. 3

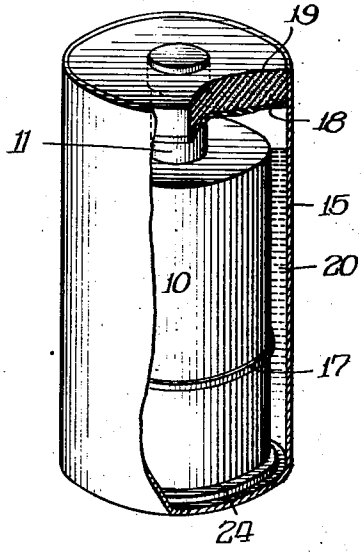
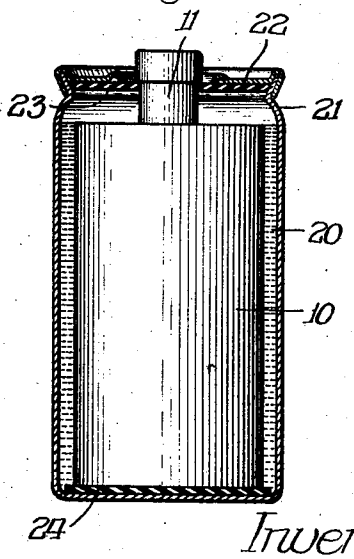


Fig. 4



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DRY CELL, CORE THEREFOR, AND METHOD OF PRODUCING SAME

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20 Claims. (Cl. 136—123)

This invention relates to improvements in dry cells and their method of manufacture and is applicable to that type of dry cells which have a central core comprising a carbon pencil and a compressed mass of depolarizing material; and in the manufacture of which the core is fabricated as a separate unit and then put into operative association with the zinc can by means of a gelatinous electrolyte surrounding the core and occupying the space between the core and the zinc can.

The depolarizing material of the cores referred to, is usually composed of a mixture of manganese dioxide, carbonaceous material, ammonium chloride, zinc chloride, and water, and such cores are usually formed by preparing the mixture as a damp, fairly cohering mass and then compressing the same around the carbon pencil so that the latter is centrally disposed in the core.

The moldable character of the material enables the formation of good cores by compression but irrespective of how well formed they may be, such cores, nevertheless, are relatively fragile and when inserted into a zinc can, which has a relatively sharp upper edge, portions thereof are likely to fall, or to be scraped or broken off. Also there is the further danger of partial disintegration of the core, or a washing off of loosely adhering crumbs or particles when the core is brought into contact with the ungelatinized electrolyte mixture and before the electrolyte is converted to a relatively stiff gelatinuous consistency.

The maintenance of the physical form of the core and the prevention of its disintegration after it has been placed in the zinc cup are essential to the production of satisfactory commercial cells, as the scaling off of particles of depolarizing material and the collection thereof adjacent the bottom of the cell between the core and the zinc cup, will cause short circuits in the cell or establish local action therein, either or both of which will entirely destroy the usefulness of the cell as a commercial product, or so materially shorten its life that it will fall below the standards now demanded for dry cells in use.

In prior commercial practice, it has been customary to maintain the physical form of the core by means of a wrapping of cheese cloth or some similar material. Such cloth or material has been found to be well suited for the purpose as it retains the core particles while at the same time it readily passes the electrolyte mixture so that the latter intimately contacts the core without causing objectionable air films to be formed therebetween. However, cheesecloth and such other materials are relatively expensive and their use adds materially to the cost of the cell particularly as the wrapping operations are both time consuming and costly.

It is an object of the present invention to provide a novel type of core and a method of producing the same, which will entirely dispose of and render unnecessary, the use of any type of wrapping for the core, or in other words, which will result in an unwrapped core which can be placed directly into the zinc cans without the danger of suffering the disadvantages which have heretofore been encountered in the manufacture of dry cells.

By means of this invention, all of the above indicated requirements for dry cells have been fulfilled and in addition, certain new advantages are realized, all of which will become readily apparent to one skilled in this art from the following description outlining several methods of manufacture that may be employed and the characteristics of the finished cells resulting therefrom.

In general, the advantages of this invention are accomplished by certain manufacturing steps hereinafter described in detail which result in the formation of a hardened casing on the core whereby the core is rendered strong and resistant so as to be free from the danger of breaking or having portions scraped off or disintegrated during placement of the core in the can and its engagement with the electrolyte therein.

The hardened casing for the core is supplied by the deposition throughout a small region adjacent the surface of an amount of a crystallizable substance such as sal ammoniac which is already present in the core as a constituent of the depolarizing mixture. It is found in practice, that such deposition which is in all probability a recrystallization of the sal ammoniac, can be effected by the various steps hereinafter described so that at least a portion of the sal ammoniac present in the depolarizing mixture serves as a strengthening material rendering the core relatively hard and tough on its surface and throughout a small portion of its depth below the surface.

The sal ammoniac as ordinarily employed in admixture with the other ingredients of the depolarizing mixture, and a quantity of water, is not of such physical form as to exert a harden-

ing and strengthening influence upon the compressed core. However, it has been found that when sal ammoniac is deposited from solution as by the removal of moisture that it is recrystallized, and as thus deposited, it exerts a hardening and strengthening influence acting somewhat as a hardened and dried binder which renders the surface of the core relatively tough and resistant.

Although it is not necessary, an amount of sal ammoniac in the depolarizing mixture in excess of that ordinarily employed may be added, in order to increase the hardening action, but the practice of this invention requires merely that a portion of the sal ammoniac ordinarily employed be deposited from solution as by a drying or heating action. In other words, the invention is predicated upon the principle of converting a suitable substance such as a certain portion of the sal ammoniac present in the depolarizing mixture throughout the region of the core adjacent the surface thereof to that physical form which results from being deposited from solution whereby to form a hardened case on the core of such character as to render the use of wrappings unnecessary.

Accordingly, one form of the invention involves, in addition to the usual practice of manufacturing cores of this type, the step of subjecting the compressed cores to a suitable drying action. In accordance with this method, the cores are made in the usual way, preferably in a tamping machine and may then be subjected to a suitable cleaning action. It is known that cores as ejected from the tamping machine frequently have attached to them, loosely adhering particles or crumbs and also thin fins of core material adjacent the top and bottom thereof. These loose particles and fins are therefore brushed off by means of a long bristled brush of such construction and by such operation that all of the loose particles and fins are properly removed without subjecting the core to the danger of being broken or deformed. This practice is necessary only when the cores are not clean and smooth when taken from the tamping machine. The cores in this form may then be exposed to a drying atmosphere which may be at ordinary temperatures for a prolonged period, such as for a number of hours, a day, or perhaps over night so that a portion of the sal ammoniac, which is embodied as an ingredient of the depolarizing mixture will be caused to be deposited by the evaporation of moisture throughout the surface region of the core for a slight depth thereof immediately underlying the surface.

Another form of this invention involves the deposition of a suitable substance, such as sal ammoniac by subjecting the cores after the cleaning operation to a gentle and uniformly warming heat for a period of a few minutes. The cores are then allowed to stand and cool to room temperature or slightly above room temperature, with the result that sal ammoniac is deposited to form the relatively hard and tough layer on the outer surface of the core and for a slight portion of its depth underlying the surface. This last method involving the application of heat is found to accomplish the desired results more rapidly than the exposure method, and in some instances, more satisfactorily. It is found that the latter practice causes a greater deposition of the sal ammoniac in the crystalline or hardening form because, due to the heat, a larger portion thereof is taken into solution in the moisture present in the depolarizing mixture. It is well known that many materials are soluble in water to a larger degree at elevated temperatures wherefore in the present case the increased temperature, due to the heating action, causes a larger portion of the sal ammoniac to be dissolved and, consequently, thereafter, to be deposited during the drying and cooling treatment following the heating step.

Furthermore, the heating of the cores may be carried out in an atmosphere of such humidity that no evaporation takes place, in which case the hardening of the core is accomplished only as the result of the dissolution and recrystallization of a portion of the sal ammoniac as above described.

The cores thus treated may then be inserted into the cans which are preferably provided with flat washers usually of paraffined paper, placed in the bottom thereof and which contain a sufficient amount of the liquid electrolyte to bring the level of the electrolyte approximately to the level at the top of the core when the core is placed within the can.

In order that the cores may be satisfactorily centered in the can, so as to avoid the danger of the core touching the zinc walls of the can, and also so as to assure an approximately uniform thickness of the electrolyte surrounding the core, a temporary spacing device in the form of a collar which engages the rim of the can and the projecting end of the carbon pencil may be placed in engagement with the pencil and the can, as shown in the drawing. The zinc can with its contents may now be heated as by placing it in hot water for the purpose of gelatinizing the electrolyte mixture to convert it from a liquid consistency into the consistency of a paste. After the paste has partially or completely set, the spacer may be removed and the cell finished in any suitable way such as by means of a washer supporting a wax seal or by means of a mechanically applied crimped-on closure.

As an alternate procedure, especially in the case of cores that are relatively long in proportion to their diameter, and especially when it is desirable to take additional precautions against short circuiting by the core touching the zinc can at or near the bottom thereof, a rubber band may be placed around the waist of the core a short distance from the bottom so as to serve as a spacer between the core and the wall of the can for effectively maintaining a space therebetween equal to the thickness of the rubber band.

By means of this invention it is possible to make high-grade dry cells at a greatly reduced cost, since all inactive materials which have been heretofore used as wrappings or coatings for the core have been dispensed with, as well as the expensive labor and material required for applying such wrappings. This change results in a substantial and important saving in the manufacture of cells. Another saving results from the elimination of various shapes and sizes of cardboard spacers, together with the elimination of the cost of manufacturing and applying such spacing devices. Furthermore, greater efficiency of the cell is realized because the elimination of the wrapping or substitute covering material leaves more room within the limited volume of the can for active materials constituting the battery and thus larger battery capacities are produced with cans of the same size or the same battery capacity with cans of smaller size.

The method of practicing this invention will

be more fully appreciated by referring to the accompanying drawing in which:

Figure 1 is a perspective view partially broken away of a core made in accordance with the present invention;

Figure 2 is a side elevational view in cross section illustrating the core and its associated cam together with the spacing element which is used during the assembly operation for accurately assembling the cell;

Figure 3 is a perspective view partially broken away to disclose the relationship of the parts of a cell manufactured in accordance with this invention and closed by a washer and sealing material; and

Figure 4 is a side elevational view in cross section illustrating a cell manufactured in accordance with this invention and closed by means of a crimped-on top.

By referring to the drawing, it will be noted that Figure 1 shows a compressed core **10** including an imbedded carbon pencil **11** and made up in the usual way in cylindrical form, and composed of the usual constituents employed for depolarizing mixtures. However, as disclosed by the portion broken away showing the interior of the core, the region **12** adjacent the surface of the core, is hardened by means of the recrystallization of a substance contained in the mixture, such as sal ammoniac so that the surface region of the core is relatively tough and resistant and can be used without being wrapped and without suffering the likelihood of damage heretofore encountered in the manufacture of cells of this type.

As a specific example of the method of producing this improved core, the cores, after being tamped and cleaned may be heated by passing the same through an electrically heated oven which in practice has been found to give good results when it is approximately five feet long. Also it serves well to have the oven open at both ends so that a steel conveyor may enter at one end and leave at the opposite end. The cores may be placed on the conveyor in upright position on rather heavily enameled wire screen pieces which may be attached by special links occurring at intervals of about one foot apart, along the length of the conveyor. The oven may be heated by hot air supplied from below the screen sections of the conveyor so that the hot air will rise and in so doing come in intimate heating contact with the cores. The air may be heated by any suitable means such as by electrical heating elements placed in the lower regions of the oven. The speed of the conveyor may be adjusted to cause the cores to remain in the oven for approximately five minutes and the heat of the oven may be adjusted to a temperature of approximately 350 degrees F.

It is to be understood that the term sal ammoniac as used herein is intended to include either ammonium chloride or the double chloride of ammonium and zinc. An inspection of the core after the heating and drying treatment reveals that the recrystallized particles of sal ammoniac are not readily apparent on the surface of the core but if the core is broken, it will be found that the crystals are deposited throughout the outer region of the core for a depth of approximately $\frac{1}{32}$nd to $\frac{1}{16}$th of an inch, thus forming the relatively hard and tough layer, which however, again becomes moistened when the core is brought into contact with the ungelatinized electrolyte. At this time, however, the assembling operations likely to cause damage are completed and immediately after the remoistening of the core, the electrolyte is converted by the action of heat to a paste consistency which prevents the liability of disintegration of the core such as would be apt to cause damaging short circuits or the like.

It is to be understood that this invention is not to be limited to the use of sal ammoniac or any particular material which crystallizes out of the depolarizing mix as any other well-known substance which will undergo the same or a similar action will serve equally well and is contemplated for use in practicing this invention.

As shown in Figure 2, the centering of the core may be accomplished by means of a temporary spacing device **13**, which may be made of any suitable material, such as wood or the like, and which has the overhanging edge **14** for closely engaging the upper end of the can **15** and the central hole **16** for snugly engaging the upper end of the carbon pencil **11**. Although spacing devices of this kind have been used in the past in the manufacture of cells of this type, it is contemplated that with the use of the unwrapped cores of this invention, that the same may be made to have a closer and more accurate fit with the can and carbon pencil.

It is further contemplated that a rubber band **17** may be used as shown in Figure 3, serving as a spacer around the waist of the core. In Figure 3, the finished cell is represented as closed by means of an insulating disk **18**, and sealing material such as sealing wax **19**, formed on top thereof.

The electrolyte occupying the space between the can **15** and the core **10** is of usual composition and is represented at **20** in Figures 2 to 4 inclusive. It is also noted that an insulating disk **24** is provided in the bottom of the can to prevent the core from contacting directly the bottom zinc wall thereof.

Figure 4 represents an alternative form of closure which requires a modified type of can having the inwardly extending top edge **21** and a metallic crimped-on closure **22**. In this form, an insulating disk **23** underlies the closure **22** and engages at its outer edge, the wall of the can and at its inner edge, the carbon pencil projecting from the core. It will be noted that the closure **22** has an enlarged opening **23** centrally thereof, so as to permit the outward passage of the pencil without danger of short-circuiting contact with the can.

When the invention is practiced by heating the cores, it is to be understood that an increased amount of sal ammoniac is deposited for hardening the surface region thereof. It is known that sal ammoniac is soluble to the extent of approximately 30 parts by weight, in 100 parts by weight of water, at ordinary temperatures and to the extent of 77 parts by weight in boiling water. It is not thought that this soluble relationship is substantially altered by the presence of zinc chloride. It will thus be seen that under the influence of the increased temperature effected by the heating oven, a larger amount of sal ammoniac is taken into solution and thus a larger amount is recrystallized during the subsequent cooling and drying treatment.

We claim:

1. The method of producing cores for dry cells which comprises providing a depolarizing mixture having therein a substance which acts electro-chemically as an ingredient of said mix-

ture and which is water soluble and capable of being deposited from solution to exert a hardening and toughening effect upon the particles of said depolarizing mixture, rendering said mixture moldable by the addition of water, forming said core, and thereafter causing evaporation of said water to an extent which causes deposition of said electro-chemically active substance in amount sufficient to provide a relatively hard and tough casing for said core consisting of said electro-chemically active substance.

2. The method of producing cores for dry cells which comprises providing a depolarizing mixture having therein a substance which acts electro-chemically as an ingredient of said mixture and which is water soluble and capable of being deposited from solution to exert a hardening and toughening effect upon the particles of said depolarizing mixture, rendering said mixture moldable by the addition of water, forming said core, and thereafter subjecting said core to a drying action whereby said electro-chemically active substance is deposited from solution throughout the dried outer region of said core and provides a relatively hard and tough casing for said core consisting of said electro-chemically active substance.

3. The method of producing cores for dry cells which comprises providing a depolarizing mixture having therein a substance which acts electro-chemically as an ingredient of said mixture and which is water soluble and capable of being deposited from solution to exert a hardening and toughening effect upon the particles of said depolarizing mixture, rendering said mixture moldable by the addition of water, forming said core, and thereafter subjecting said core to a heating action to increase the solubility of said substance and finally cooling and drying said core to deposit said electro-chemically active substance from solution throughout the outer region of said core so that said electro-chemically active substance as deposited provides a relatively hard and tough casing for said core consisting of said electro-chemically active substance.

4. The method of producing cores for dry cells which comprises providing a depolarizing mixture having a quantity of sal ammoniac therein, rendering said mixture moldable by the addition of water, forming said core, and thereafter causing evaporation of said water to an extent which causes deposition of a portion of said sal ammoniac in amount sufficient to provide a relatively hard and tough casing for said core consisting of said sal ammoniac.

5. The method of producing cores for dry cells which comprises providing a depolarizing mixture having a quantity of sal ammoniac therein, rendering said mixture moldable by the addition of water, forming said core, and thereafter subjecting said core to a drying action whereby a portion of said sal ammoniac is deposited from solution throughout the dried outer region of said core, and in such form provides a relatively hard and tough casing for said core consisting of said sal ammoniac.

6. The method of producing cores for dry cells which comprises providing a depolarizing mixture having a quantity of sal ammoniac therein, rendering said mixture moldable by the addition of water, forming said core, and thereafter subjecting said core to a heating action to increase the solubility of a portion of said sal ammoniac and finally cooling and drying said core to deposit a portion of sal ammoniac from solution throughout the outer region of said core so that a portion of sal ammoniac as deposited will provide a relatively hard and tough casing for said core consisting of said sal ammoniac.

7. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 1.

8. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 2.

9. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 3.

10. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 4.

11. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 5.

12. A core for dry cells of the type herein described adapted to be used without a wrapper thereon made in accordance with the process defined in claim 6.

13. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 1.

14. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 2.

15. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 3.

16. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 4.

17. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 5.

18. A dry cell of the type herein described, comprising a zinc can and a gelatinized electrolyte and an unwrapped core made in accordance with the process defined in claim 6.

19. The process of producing dry cells which consists in forming a core by molding a mass of depolarizing mixture which contains in its composition a substance which acts electro-chemically as an ingredient of said mixture and which is soluble in water and capable of being deposited from solution to exert a hardening and toughening effect upon said core, causing said substance to be taken into solution and thereafter forming on said core a relatively hard and tough casing consisting of said electro-chemically active substance by causing a portion of said electro-chemically active substance, throughout the region of the surface of said core to be deposited by the evaporation of moisture, thereafter placing a liquid gelatinizable electrolyte in a zinc can, placing said core in an unwrapped condition centrally of said can and insulating the same from the bottom thereof and maintaining the core so positioned while gelatinizing said electrolyte under the influence of heat, and finally, sealing the top of said can to form a completed cell.

20. The process of producing dry cells which

consists in forming a core by molding a mass of depolarizing mixture which includes in its composition, a quanity of sal ammoniac, causing a portion of said sal ammoniac to be taken into solution and thereafter causing a portion thereof throughout the region of the surface of said core to be deposited by the evaporation of moisture, in amount sufficient to provide a relatively hard and tough casing for said core, consisting of said sal ammoniac, thereafter placing a liquid gelatinizable electrolyte in a zinc can, placing said core in an unwrapped condition centrally of said can and insulating the same from the bottom thereof and maintaining the core so positioned while gelatinizing said electrolyte under the influence of heat, and finally, sealing the top of said can to form a completed cell.

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