This invention relates to the construction of electrolytic cells and more particularly, to the construction of concrete and slate cells for the production of chlorates and perchlorates.

In the past, some difficulties have been experienced with electrolytic cell containers. Electrolytic cells are preferably constructed of concrete, slate or other siliceous materials. Such materials have marked advantages over metals and other construction materials in that they are relatively inert, nonconductive, inexpensive and readily fabricated. However, concrete, slate and the like are not without disadvantages. Eventually, these materials may crack and begin to leak electrolyte and current from the cell. Also, calcium, magnesium and other salts are leached from the concrete during electrolysis and thereby contaminate the end product. Many methods have been proposed to eliminate such cracking and deterioration of the cell container.

Metal containers lined with an insulating material have been proposed, but they lack the advantages of concrete in that they may corrode due to their conductivity of electrical current. The impressed voltages result in current flow from the electrodes to metal walls and from the metal walls to ground. Thus, metal containers become electrodes and are subject to electrolytic corrosion even when only small parts thereof, such as metal bolts, contact the electrodes. Again, metal containers often create greater problem than those which they attempt to solve.

In the manufacture of alkali metal chlorates and perchlorates, the difficulties experienced in other concrete cell containers are compounded by the fact that chlorates and perchlorates may form explosive compositions with many organic materials. This is another reason for scrupulously eliminating cell leakage. Schumacher, in his book, Perchlorates, Their Properties, Manufacture and Use, ACS Monograph Series No. 146, published by Reinhold Publishing Corporation, 1960, relates at pages 187 to 220, the dangers involved in chlorate and perchlorate handling. Because of the danger of forming explosives by reaction of chlorates and perchlorates with organic materials, chlorate and perchlorate cells are commonly used in place of organic parts within such cells. In attempting to prevent cracking and eventual leakage of electrolyte from the cells, it has been the practice to line chlorate and perchlorate cells with a dense nonporous, concrete or ceramic liner. Although such liners normally retard leakage, they may eventually crack, thus prematurely ending the useful life of the cell.

It is an object of the present invention to provide a method of constructing an electrolytic cell of siliceous material internally lined with a nonconductive, inert organic liner. Another object of this invention is to provide a plasticizer useful with an organic resin, that is, inert to chlorates and perchlorates and which is useful as a liner material in electrolytic cells. It is a further object of this invention to provide a method of forming a concrete or siliceous container internally sealed with a nonconductive, plasticized, inert-resin, bonded to the interior walls thereof in a continuous manner. These and other objects will become apparent to those skilled in the art from the description of the invention.

In accordance with the invention, an electrolytic cell container is provided comprising a container having sidewalls and a bottom of siliceous material and having bonded to the interior of said sidewalls and bottom a liner comprised of an inert organic resin plasticized with a plasticizing amount of an organic plasticizer, said resin and plasticizer combination being inert to reaction with alkali metal chlorates and perchlorates.

The present invention provides electrolytic cells with an impervious liner which is sufficiently flexible, resilient and elastic to withstand the stresses within a cell created by expansion, contraction and even the cracking of the siliceous walls and bottom without rupturing. Such a liner is capable of sustaining the stresses created by thermal expansion due to temperature changes and is sufficiently elastic to retain its continuity without rupture in the event that the supporting siliceous material should eventually crack. The liner is bonded to the siliceous container by means which eliminate the attaching studs, bolts, etc., which pierce the liner thereby breaking the continuity of the liner. Further, the liner and plasticizing materials used are those which are inert to reaction with chlorates and perchlorates, in addition to being inert to normal electrical and chemical attack.

The invention will be described with reference to the drawing which is a sectional view of an electrolytic cell made in accordance with the present invention.

The electrolytic cell shown is composed of electrodes 22 located in container 10. Container 10 has sidewalls 12 and bottom 16 constructed of a siliceous material and a top 24 which may also be of siliceous or other inert material. The interior of the rigid siliceous material is lined with a plasticized resin liner 14 bonded to the sidewalls 12 and bottom 16. The liner 14 covering bottom 16, preferably has an electrode support base 18 placed over it. Placed or attached to electrode support base 18, is electrode container 26. Electrode container 26 contains the electrodes 22, and has openings (not shown) which permit the flow of electrolyte in and out thereof. In the operation of the cell, the container 10 and electrode container 26 is filled with electrolyte.

The material of which the cell walls 12 and bottom 16 are constructed in an inert siliceous material such as concrete, cement, slate, ceramic, glass, and the like. Therefore, the term siliceous material means concrete, cement, slate, ceramic, glass, and the like materials.

The plasticized liner 14 is a nonconductive plasticized resin inert to conditions existing within the cell under both operating and standby conditions. As used herein, the term "inert plasticized resin" and "resin" means a synthetic organic polymer as polyvinyl chloride resin, polyvinylidene chloride resin, after chlorinated polyvinyl chloride resin and the like halogenated polymeric resins inert to chlorate and perchlorate attack, said resin containing a plasticizing compound, the combination of plasticizer and resin being substantially nonconductive of electricity and inert to chlorate and perchlorate attack.
The plasticizers useful with the named resins are those which impart certain physical and chemical characteristics to the compounded resin. There are numerous commercial plasticizers available. Available plasticizers include esters, aromatics, ketones, phosphates, ethers, halogens and epoxides. Certain groups of these plasticizers are useful in the present invention as well as certain individual plasticizers. A plasticizer resistant to chlorate and perchlorate reaction is one which is also resistant to hydrolysis. Resistant to hydrolysis means the plasticizer resists decomposition when refluxed in ten percent sulfuric acid at the boiling point for a minimum of 100 hours. In addition to being resistant to hydrolysis, physical characteristics of the compounded resin as to elongation, tensile strength and tear strength, further delineate the group of plasticizers which are useful.

Susceptibility to hydrolysis is a convenient test to determine the plasticizers and plasticized resins which will be unaffected by chlorate and perchlorate attack. Alternatively, the plasticized resin can be tested directly by attempting to react a solution of sodium chlorate and/or sodium perchlorate with the plasticized resin. The plasticized resins are subjected to solutions of chlorate and perchlorate for two to seven days. The resin sample is then dried and subjected to impact, flame and heat tests to determine whether the plasticized resin is acceptable for use. Those plasticized resins which exhibit properties which could create a fire or explosive danger based on the results of the tests are unsuitable for use in the present invention. The plasticizers which meet the chemical and physical requirements of the present invention are halogenated plasticizers such as chlorinated biphenyls and polyphenyls, halogenated and nonhalogenated polyester resins, especially those having molecular weights averaging 800 to 3500, phosphates such as cresyl diphenyl phosphate and tri cresyl phosphate, halogenated paraffins such as pentachloroethane, heptachlorotetra-cosane, octachloroethane, and the like, and aromatic, polyaromatic and arylalkyl hydrocarbon esters such as dioctylphthalate, di-n-octylphthalate, di-iso-octylphthalate, etc., having molecular weights averaging 250 to 700. These plasticizers can be used singly or in combination with each other, the preferred plasticizers being those which are relatively nonflammable in combination with the resin. Thus, a flammable plasticizer can be used in combination with a nonflammable plasticizer such as a phosphate or halogenated compound to provide a plasticizer which is substantially nonflammable in the plasticized resin so as to be considered self-extinguishing.

The plasticizer is compounded, milled, and otherwise processed, in a plasticizing amount with the resin, so as to impart to the resin a modulus of elongation, as measured by American Society for Testing Material (ASTM) method D-638–52T, of at least 200 percent. The maximum elongation is normally not more than 500 percent. The amount of plasticizer used varies with the particular plasticizer but normally is in an amount of about 1 to 50 percent by weight of the compounded resin, and most preferably 20 to 50 percent by weight of the compounded resin. In addition to the plasticizer, which may be a combination of the stated plasticizers, fillers such as titanium dioxide, mica, asbestos, silica, and the like, inerts, may be used. Such fillers are preferably not used in excess of about 5 to 10 percent based on the total weight of the compounded resin.

The plasticized liner is applied directly to the silicous cell container in an amount sufficient to seal the cell container and provide a barrier impervious to electrolyte and electric current. Such applied liner is used in a thickness and strength sufficient to withstand expansion and contraction without rupture. Also, the resin is applied in an amount sufficient to provide strength to span cracks, ruptures, etc., which may subsequently develop in the silicous container material. The proper film thickness is determined for the particular compounded resin as that providing a tensile strength of 500 to 2500 pounds per square inch determined by ASTM method D-638–52T. In addition, the film thickness is that which provides a tear strength, as measured by ASTM method D-624–54, of from 100 pounds per square inch to about 600 pounds per square inch. It has been found that a film applied in an amount ranging from about 15 mils to about 100 mils, and more preferably in an amount of about 45 mils to 75 mils is suitable to meet the preferred physical characteristics and to thereby withstand the stresses created by the expansion and contraction due to the operation of the cell. The resin liner is permanently bonded directly to the silicous container material. This is accomplished by either coating, brushing or spraying, the plasticized resin in a solvent onto the contained walls, or more preferably by bonding a preferred sheet of plasticized resin material to the container by means of an adhesive.

The adhesive is used is any adhesive capable of bonding the plasticized resin to the silicous container walls. A preferred adhesive is a solution of polyvinyl chloride in a solvent such as tetrahydrofuran. The adhesive is applied to both the container and the resin sheeting.

The adhesive is allowed to dry to a tacky state prior to positioning the resin sheet over the container walls and smoothing it into place.

In addition to the plasticizers and fillers that may be used in the compounded resin sheeting of this invention, reinforcing, such as a fiberglass backing, can be used with the resin sheeting. Such backing is desirable in that it aids in forming a more adherent surface for the adhesive. Also, the tensile strength of the resin sheeting is thereby increased.

The following examples illustrate certain preferred embodiments of the present invention. Unless otherwise indicated, all parts and percentages are by weight.

**EXAMPLE 1**

A concrete cell container was lined with a plasticized polyvinyl chloride resin reinforced with a glass fabric backing in accordance with the present invention as follows:

A cell containing having sidewalls and bottom totaling about 900 square feet was lined by applying sheets, 60 mils thick, to the internal walls and bottom of the concrete container. The polyvinyl chloride sheeting was Quelcor 1093. This material was composed of 53 percent polyvinyl chloride, 43 percent plasticizer, 4 percent filler, and had a glass-fiber backing. The compounded resin had a Durometer Shore A Hardness as determined by ASTM method D–676–49T of 80. The modulus of elongation was 320 percent, the tensile strength was 1900 pounds per square inch and the tear strength was 275 pounds per square inch.

Prior to applying the polyvinyl chloride sheeting, the inside surface of the cell container was conditioned by removing the loose particles and filling all deep pits, gouges and cracks and provident. The contaminated surface was then etched with a ten percent solution of muriatic acid. An adhesive solution of polyvinyl chloride in tetrahydrofuran was then applied to the concrete surface and to the glass-fiber backing on the polyvinyl chloride sheet. The adhesive was allowed to dry to a tacky condition. The sheeting was then rolled onto the concrete surface in a manner such that the air entrapped between the sheet and the concrete surface was removed. The side walls and the bottom of the cell container was lined in this manner.

Having secured the polyvinyl chloride sheeting, the seams between the applied sheets were heat sealed by
using additional strips of polyvinyl chloride resin and melting them into place. Having completely sealed the cell container with the resin sheeting, the electrode support base was cast in place on the bottom of the cell container using a low slump concrete mix. After curing the support base, the electrode container was attached to the base support as shown in the drawing.

The electrolytic cell containers prepared in this manner were subsequently used for the electrolysis of sodium chloride to sodium chlorate. Also, similar containers prepared in the same manner were used for the electrolysis of sodium chloride to sodium perchlorate. After continued use for a period of 18 months, no failure or leakage was detected. Examination of the plasticized resin liners did not reveal degradation or chemical or electrical attack thereof.

EXAMPLE 2

A slate cell container was lined with a plasticized polyvinyl chloride resin by the method of Example 1. Polyvinyl chloride sheeting of 50 mil thickness was prepared by milling 65 percent by weight of polyvinyl chloride with 35 percent by weight of a chlorinated biphenyl plasticizer called Aroclor 1232.

The sheeting was bonded to the slate using polyvinyl chloride resin in solution with tetrahydrofuran as the adhesive. The seams between the applied sheeting were sealed by melting additional strips of polyvinyl chloride over the seams. The resulting cells were impervious to liquid and particularly resistant to chemical attack by chlorates and perchlorates.

In addition to the resin compositions described in the examples, other plasticizers in various plasticizing amounts are useful, within the described limits, particularly halogenated biphenyls and polyphenyls, halogenated paraffins, halogenated polysters, organic phosphates and aromatic, polyaromatic and aryl alkyl hydrocarbons. These plasticizers are additionally used with after-chlorinated polyvinyl chloride, polyvinylidene chloride and the like halogenated polymers.

Although the invention has been described more particularly for use with chloride and perchlorate production, it is to be noted that the use of the described cells, lined with the plasticized resins described, are also useful with concrete cell containers for other processes. Such liners greatly prolong the life of the cell containers, reduce maintenance costs, in addition to reducing losses of products due to leakage and reducing the loss of electric current from the electrolytic cell.

While there have been described various embodiments of the invention, the apparatus of methods described are not intended to limit the scope of the invention as it is realized that changes therein are possible within the invention. It is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized.

We claim:

1. An electrolytic cell for the production of chlorates and perchlorates comprising a container having sidewalls and bottom of siliceous materials selected from the group consisting of concrete, cement, ceramic, glass and slate, said container being internally lined with a plasticized resin selected from the group consisting of polyvinyl chloride, polyvinylidene chloride and after-chlorinated polyvinyl chloride, said plasticized resin being inert to reaction with chlorates and perchlorates, said lining being bonded to the internal sidewalls and bottom of said container, said container having therein an electrode support base disposed on the liner covering the bottom of said container thereby providing a support for the attachment of electrodes, and electrodes in an electrode container attached to said support base, said electrode container having openings for electrolyte circulation.

2. The electrolytic cell of claim 1 in which said resin is polyvinyl chloride.

3. The electrolytic cell of claim 1 in which the plasticizer resin composition is inert to hydrolysis and substantially self-extinguishing.

4. The electrolytic cell of claim 1 wherein the plasticized resin is applied in an amount equal to a film thickness of 15 to 100 mils.

5. The electrolytic cell of claim 1 wherein the plasticized resin is applied in an amount equal to a film thickness of 45 to 75 mils, said film having a modulus of elongation of 200 to 500 percent, a tensile strength of 500 to 2500 pounds per square inch and a tear strength of 100 to 600 pounds per square inch.

6. The electrolytic cell of claim 1 wherein the plasticized resin composition has a glass fiber reinforcing.

7. The electrolytic cell of claim 1 wherein the plasticized polyvinyl chloride resin contains 25 to 50 percent plasticizer.

8. In the production of a member selected from the group consisting of alkali metal chlorates and perchlorates by the electrolysis of a corresponding precursor, the improvement which comprises separating the electrolyte from a siliceous electrolytic cell container with an essentially continuous surface of an inert, nonelectrically conductive, thermoplastic, synthetic organic polymer plasticized with a plasticizing amount of an organic plasticizer.

9. The process of claim 8 in which said synthetic organic polymer is polyvinyl chloride, applied to the siliceous electrolytic cell container in an amount equal to a film thickness of 15 to 100 mils, containing 25 to 50 percent plasticizer and said synthetic organic polymer has a glass fiber reinforcing.

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