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CORROSION RESISTANT LINING

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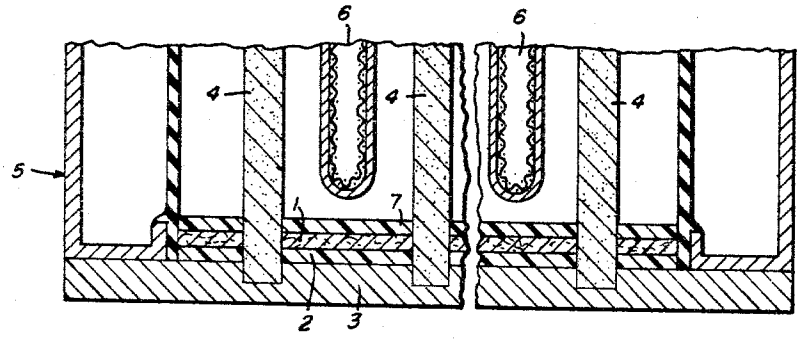


FIG. 1

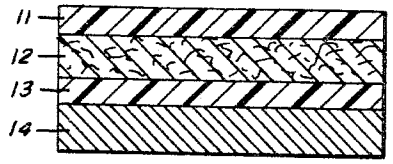


FIG. 2

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CORROSION RESISTANT LINING

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This application is a continuation-in-part of copending application Serial No. 275,645, filed April 25, 1963, now abandoned and all benefits of the latter application provided by 35 U.S.C. 120 are hereby claimed for this application.

This invention relates to corrosion resistant linings for containers of all types. More particularly, the present invention relates to a corrosion resistant lining suitable for use in linings for containers exposed to chlorine in liquid media and especially electrolytic cell parts exposed to hot chlorinated brine solutions during electrolysis.

The corrosive action of chlorine, particularly in a liquid medium, on containers is a well recognized problem in industry. A wide variety of containers for chlorine in liquid media; such as, for example, chlorate retention tanks are damaged by exposure to liquids containing chlorine. One industrial application in which corrosion of the above-described type is particularly serious is in electrolytic diaphragm cells of the alkali chlorine type. In the operation of an electrolytic diaphragm cell of the akali chlorine type, such as described in U.S. Patent No. 2,183,299, considerable difficulty is encountered in protecting the cell parts, especially at the bottom of the cell, from corrosion during the operation of an electrolytic cell of this character. Thus, in industry today many operations are performed in the preparation of the bottom assembly of a conventional diaphragm type electrolytic cell for the protection of the metallic parts located in the bottom thereof. Typically the soft metallic material, usually lead, utilized to convey current from the bus bar to the anode of the cell, is normally covered with an epoxy-coal tar composition in order to seal the metal parts from the interior of the cell. Upon completion of the sealing of the soft metal bottom, the cell is covered with a thick layer of mastic or organic sealant thus affording more protection for the metallic portions of the bottom of the cell from attack by the hot chlorinated brine during electrolysis of the akali metal chloride solutions. Another method of protecting cell bottoms is described in U.S. Patent No. 2,742,419. In this patent considerable pains are taken to provide layers of mastic and layers of grout between the soft metal conductor in the bottom of the cell and the interior of the cell.

These operations, typical of those conducted by the prior art, are quite costly and time consuming in any electrolytic cell room operation; and, in addition to requiring many man hours, also require a considerable amount of expensive material and longer graphite anodes. In disassembling a cell these prior available methods of protection cause much inconvenience especially in the removal of the protective coating from the soft metallic bottom. In order to contribute to an economical operation of the protective system the materials must be removed and separated so that they can be reused.

The foregoing disadvantages experienced in this art

have been overcome by this invention which comprises, preferably, applying an organic sealant (e.g. bituminous material) to all surfaces of a container which are to be exposed to chlorine in a liquid medium. Thus, an organic sealant is applied to the interior surfaces of the sidewalls, bottom and cover of such a container. A layer of fibrous material is then applied to the organic sealant layer before the latter is dry. The fibrous material employed in this invention is, preferably, an asbestos paper or cloth. The layer of fibrous material on the interior surfaces of the container is then coated with a layer of an organic sealant. Thereafter, the interior surfaces of the container which have been covered, as above described, are chlorinated, in situ. The chlorination of the organic sealant on the interior surfaces of the container is accomplished, preferably, by exposing the interior surfaces to hot chlorinated brine for about one-half hour, during which period the organic sealant is in contact with the said brine. The chlorinated brine is maintained at a temperature of, preferably, about 180° F. during the chlorination of the organic sealant, in situ. Chlorinated brine having a temperature from room temperature up to 212° F. may also be employed. In lieu of chlorinated brine the chlorination of the organic sealant on the interior surfaces of the container may be carried out by filling the containers with water and then bubbling chlorine gas into the water. The water may be at any temperature from room temperature up to 212° F.

This invention may be carried out in an electrolytic alkali chlorine cell, if desired. Thus, in one application of the present invention, a relatively simple method is provided for effectively lining the bottom of an electrolytic alkali chlorine cell, thus contributing considerably to an overall reduction in the economics of cell room operation. These linings of the invention last longer than prior linings to contribute to said overall economical operation. In accordance with this invention, a lining is provided which reduces considerably the man hours necessary for properly lining a cell bottom in a typical electrolytic diaphragm type akali chlorine cell and the lining is extremely resistant to the activity of hot chlorinated brines encountered during electrolysis of alkali metal chloride solutions.

Thus, it has been found that by spraying the metallic portions of the bottom of an electrolytic akali chlorine cell with an organic sealant (e.g., bituminous material), affixing to the sealant prior to its drying a sheet of inert fibrous material such as asbestos paper or cloth, and coating the inert fibrous material with sealant, then an effective lining is presented to the hot chlorinated brine solutions encountered is electrolytic cell operation.

In practice it is desirable to prepare the lining by providing at least two coats of organic bituminous sealant on the surface to be lined or with sufficient sealant to cover the surface prior to affixing the asbestos or other inert fibrous material to the surface of the sealant and then applying a coat of sealant to the surface of the inert fibrous material. Thus, in one mode of providing linings in accordance with this invention, an organic bituminous sealant, such as Coal Cat (a coal tar-epoxy resin manufactured by the Pittsburgh Plate Glass Company, Pittsburgh, Pennsylvania) is applied to the surface or bottom of an alkali chlorine cell. The organic bitmuinous sealant layer placed thereon is permitted to harden and upon harden-

ing a second layer of the sealant is applied. Prior to complete drying of the second layer of sealant, asbestos paper or cloth is laid upon the surface of the sealant and sufficient pressure applied to the paper until all air under the fibrous material is eliminated and to assure adequate adhesion of the paper to the organic sealant underlying it. After the asbestos is sufficiently adhered to the sealant it is coated with a layer of sealant. Upon completion of this operation, the cell is assembled in its entirety and brine is admitted to the chamber and permitted to wet the asbestos-sealant surface. The cell is then placed in operation and the electrolysis of the brine produces chlorine in the brine. The chlorine-containing brine chlorinates the asbestos-organic sealant layers on the interior surfaces of the cell, in situ. Upon further electrolyzing the brine solution contained in the cell, it is found that essentially little or no corrosion takes place underneath the asbestos lining.

The brine solution used is that normaly encountered in an electrolytic chlorine cell. It consists of 250 grams per liter NaCl, saturated with chlorine, at a temperature of about 195–215° F.

The utilization of asbestos forms a preferred embodiment of the present invention but the invention is not to be limited thereby since it has been found that many other materials may be utilized in lieu thereof. Thus, synthetic organic fibers resistant to brine solutions may be employed. Typical of the fibers are nylon, Orlon, Dacron, Dynel (manufactured by the United States Rubber Company) glass wool and other materials of like character. Materials such as foam glass may also be employed, the essential characteristic of the materials being that they are porous and inert. The inert porous sheet is preferably a non-woven fabric, such as a paper or felt. Tightly woven fabrics or even a sheet formed in situ, as by applying bulk inert particles, are useful.

In operation of the cell, the chlorination of the sealant extends only part way into the material. The fabric holds the chlorinated material in place so that it does not disintegrate. The chlorinated portion then forms a barrier preventing contact of the cell liquor with fresh, or unchlorinated, sealant surface. Thus, within about one-half hour of use, there is formed, in situ, in the asbestos-organic sealant cell, an outer chemically inert, chlorinated protective layer.

For a more complete understanding of the present invention, reference is made to the accompanying drawing in which:

FIGURE 1 represents the bottom of an alkali chlorine diaphragm cell with the anodes in place and the cathodes in place, the cell bottom only being shown; and

FIGURE 2 represents a typical lining of a metal surface utilizing the corrosion resistant lining of the present invention.

Turning to FIGURE 1, there is shown in the figure cell bottom **3**, which is electrically conductive and composed of a lead slab. Normally this slab rests on a concrete base (not shown) which is supported on legs to keep the cell off the cell room floor. Affixed and embedded in the lead slab are anode members **4** and these anode members rise vertically therefrom. The cathode containing member of the cell **5** contains a plurality of cell fingers **6** located between the various anode blades **4** rising vertically from the bottom of the cell. In preparing the cell bottom for utilization, two layers of sealant **2** are placed thereon, the first layer being permitted to dry completely before the second layer is superimposed on the first layer. Before completion of the drying of the second layer of the organic bituminous sealant, preferably an epoxy resin-coal tar mixture, an asbestos paper lining **1** is placed thereon and sufficient pressure is placed upon the paper during its initial contact with the organic bituminous sealant to assure complete adherence of the paper to the sealant and until all air under the fibrous material is eliminated. After the asbestos is sufficiently adhered to the sealant it is coated with a layer of sealant **7**.

FIGURE 2 indicates the lining of the present invention placed upon a structural material surface **14**, specifically steel, in which the sealant **13** is affixed to the steel surface, the asbestos paper **12** is adhered to the sealant **13** and a surface coating of sealant **11** is adhered to the asbestos paper **12**.

The lining of the present invention has particular utility in the operation of electrolytic cells of the diaphragm type since it is extremely inexpensive to apply, may be readily applied with complete safety, and requires no special handling equipment. Contrary to the practices currently conventional in the art, a low-cost, relative rapid method of providing suitable corrosion resistant lining for the operation of an alkali chlorine cell is thereby provided. In addition to utilization in the operation of alkali chlorine cells of the diaphragm type, it is, of course, obvious that the lining of the present invention may be employed in a wide variety of uses. Thus, the lining may be readily employed in retention tanks in the operation of chlorate cells. It may be utilized to line surfaces exposed to chlorinated brines, such as cover and side members for alkali chlorine cells and other similar applications.

For a more complete understanding of the present invention, reference is made to the following examples which typically illustrate the corrosion resistance of linings prepared in accordance with the teachings hereinbefore set forth:

EXAMPLE 1

A cylindrical steel disc 1 inch in diameter and 2 inches long is sprayed with an application of Pittsburgh Plate Glass Company Coal Cat, an epoxy resin-coal tar sealant composition. After the initial layer of the Coal Cat material has hardened, a second application of the Coal Cat is applied to the metal disc. Prior to the solidification of the second layer of the Coal Cat, a sheet of asbestos paper is affixed to the surface of the sealant and pressure applied to assure complete adherence of the paper to the sealant and expulsion of all air from under the asbestos paper. The exposed surface of the asbestos paper is then coated with a layer of Coal Cat sealant. After the organic bituminous sealant has hardened, it is wetted with unchlorinated brine and the disc is placed in an operative alkali chlorine cell of the type described in U.S. Patent No. 2,183,299. The cell is operated continuously in a production line for a period of four months. Upon completion of a four-month period of operation, the disc is removed from the cell and examined for corrosion. Visual examination of the disc shows no corrosion to have taken place.

EXAMPLE 2

One or more coats of Laminac 4107, a polyester resin, as sealant were applied to the pickled surface of a cylindrical steel disc 1 inch in diameter and 2 inches long until the steel was thoroughly covered. After this protective coat(s) had been allowed to dry, another coat was applied. While this coat was still wet, the fibrous material was laid on the wet film and was pressed in until all air under the asbestos was eliminated. Additional sealant was then applied over the fiber until the desired thickness of protective covering was obtained. No fibrous or porous material was exposed to the cell solution. The cell brine solution consisted of 250 grams per liter NaCl, saturated with chlorine, at a temperature of about 195–215° F.

Tests were made on steel plugs coated with particular resins and fibrous materials, in a chlorine brine solution in order to determine the best composition of lining to be used in the electrolysis chlorine cell. The fibrous materials tested were cotton, Dacron and Dynel. Dacron is a condensation polymer of ethylene glycol with terephthalic acid, Whinfield Patent 2,465,319 and Dynel is a copolymer of vinyl chloride and acrylonitrile used as a textile fiber. Laminac 4107, Haveg 7010 and Haveg 7710 are polyester resins.

In general, the sealant can be any one of the many polyester resins, epoxy resins and bituminous materials, including those modified with epoxy resins. U.S. Patents 2,514,141 and 2,726,223 give examples of the polyester resins that could be used. Greenlee Patent No. 2,694,694 illustrates the epoxy resins that could be used. U.S. Patent 2,765,288 is representative of the bituminous material suitable for use in the composition of the invention. As may be seen, the organic resin sealants include synthetic resin sealants.

EXAMPLES 3–13

Exposure of coated steel plugs to chlorine cell anolyte

Example	Coating Construction—Sealant+fibrous sheet+impregnant if used	Total Time of Test	Remarks
3	Coat Cat+Dacron	3 weeks	Good condition.
4	Haveg 7010+Cotton	5 weeks	Do.
5	Haveg 7010+Cotton	7 months	Failed.
6	Laminac 4107+Dynel	8 months	Excellent.
7	Laminac 4107+Dacron	do	Do.
8	Haveg 7010+Dacron	8½ months	Failed.
9	Haveg 7010+Dynel	11½ months	Do.
10	Haveg 7710+Dynel+Haveg 7710	3 months	Excellent chlorinated surface quite hard and strong.
11	Coat Cat+Dynel+Coal Cat	do	Excellent. Surface a little soft.
12	Haveg 7710+Crocidolite Asbestos Paper+Haveg 7710.	do	Excellent. Surface quite hard and strong.
13	Coat Cat+Crocidolite Asbestos Paper+Coal Cat.	do	Good. Surface a little soft.

In Examples 3, 7 and 8, "Dacron" is the trademark for a synthetic polyester fiber made from methyl terephthalate and ethylene glycol and in Examples 6, 9, 10 and 11 "Dynel" is the trademark for a fiber made from a copolymre of vinyl chloride and acrylonitrile.

In the above Examples 3–13, the steel discs were first coated with one or more coats of sealant until the steel was thoroughly covered. After this protective coats(s) had been allowed to dry, another coat was supplied. While this coat was still wet, the fibrous material was laid on the wet film and pressed in until all air under the fibrous material was eliminated. Additional sealant was then applied over the fiber until the desired thickness of protective covering was obtained.

EXAMPLE 14

A disc similar to those used in the previous examples was coated with three layers of Haveg 7710 Polyester. The surface layer of polyester was then exposed to the cell brine for three months, removed, examined and found to have failed.

EXAMPLE 15

Another disc was prepared and tested as in Example 14 except that three layers of Coal Cat were used instead of Haveg 7710 Polyester. In this test the protective layer also failed after three months.

EXAMPLE 16

The interior surfaces of a container for an aqueous medium containing chlorine were coated with a layer of the epoxy resin-coal tar sealant (Pittsburgh Plate Glass Company Coal Cat) employed in Example 1. When this layer hardened, a second layer of the Coal Cat sealant was applied to the interior surfaces of the container. Prior to solidification and hardening of the second layer, a layer of asbestos paper was applied to each interior surface of the container and pressure applied to expel air from between the paper layer and the underlying layer of Coal Cat sealant. The exposed surface of the asbestos paper was then coated with a layer of Coal Cat sealant and this outer layer of sealant was hardened. The container was then filled with a hot chlorinated brine (about 180° F.) and the exposed surfaces of the outer layer of the Coal Cat sealant were maintained in contact with the hot chlorinated brine for about one-half hour to chlorinate the outer layer of organic sealant, in situ. The chlorinated portion of the outer layer of organic sealant provided a protective barrier which prevented the underlying layers from being attacked by chlorine in a liquid medium stored in the container.

EXAMPLE 17

The method described in Example 16 was carried out in the manner described except that the tank was filled with water in lieu of hot chlorinated brine. The water was maintained at a temperature of about 180° F. and chlorine gas was bubbled into the hot water for one-half hour. The outer layer of organic sealant was chlorinated, in situ, and thus rendered resistant to the attack of chlorine in a liquid medium stored in the tank.

Other methods of applying a protective coating to a metal surface are useful, although the above-described construction is preferred. The metal surface is coated with one or more coats of sealant or until the surface is thoroughly covered. The inert fibrous material is then affixed with sufficient pressure to expel all air from under it. Another way is to sufficiently cover the surface to be protected with sealants and then affix with pressure an inert fibrous material which had been previously saturated with sealant. Still another way is to liberally coat the surface to be protected with sealant and affix the inert fibrous material with sufficient pressure to cause it to be impregnated with sealant. In these instances the surface of the fibrous material would not necessarily be additionally coated before being contacted with the brine solution.

While the invention has been described with reference to certain specific examples, it is, of course, to be understood that the invention is not to be limited thereby except insofar as appears in the accompanying claims.

We claim:

1. A metal container having on a surface to be protected a corrosion resistant inner layer of organic sealant affixed to said surface, a layer of porous inert material adhered to the organic sealant, an outer layer of organic sealant affixed to the porous inert material, and wherein said outer layer of organic sealant is chlorinated at least upon its surface.

2. A corrosion resistant electrolytic cell according to claim 1 wherein the porous inert material is fibrous.

3. A corrosion resistant cell according to claim 1 wherein the organic sealant is a bituminous sealant.

4. A corrosion resistant cell according to claim 1 wherein the organic sealant is a polyester resin.

5. A metal container according to claim 1 wherein the organic sealant is a synthetic organic sealant.

6. An alkali chlorine cell having a corrosion resistant surface comprising an inner layer of organic sealant

affixed to a surface to be protected, a layer of porous inert material adhered to the organic sealant and an outer layer of chlorinated organic sealant affixed to the surface of the porous inert material.

7. An alkali chlorine cell having a corrosion resistant surface according to claim 6 wherein the organic sealant is a bituminous sealant.

8. An alkali chlorine cell having a corrosion resistant surface according to claim 6 wherein the organic sealant is a polyester resin sealant.

9. An alkali chlorine cell having a corrosion resistant surface according to claim 6 wherein the porous inert material is asbestos.

10. An alkali chlorine cell according to claim 6 wherein the organic sealant is a synthetic organic sealant.

11. An alkali chlorine cell having a corrosion resistant surface comprising an inner layer of organic sealant affixed to a surface to be protected, a layer of porous inert material, selected from the group consisting of crocidolite asbestos fibers, synthetic polyester fibers of methyl terephthalate and ethylene glycol, and fibers of a copolymer of vinyl chloride and acrylonitrile, adhered to the organic sealant, an outer layer of organic sealant affixed to the porous inert material, and wherein said outer layer of organic sealant is chlorinated at least upon its surface.

12. The alkali chlorine cell of claim 11 wherein the outer layer of organic sealant chlorinated upon its surface is chlorinated in situ during electrolysis in said alkali chlorine cell.

13. A metal container having a corrosion resistant lining comprising an inner layer of organic sealant affixed to a surface to be protected, a layer of porous inert material, selected from the group consisting of crocidolite asbestos fibers, synthetic polyester fibers of methyl terephthalate and ethylene glycol, and fibers of a copolymer of vinyl chloride and acrylonitrile, adhered to the organic sealant, an outer layer of organic sealant affixed to the porous inert material, and wherein said outer layer of organic sealant is chlorinated at least upon its surface.

14. A corrosion resistant electrolytic cell having a corrosion resistant surface comprising an inner layer of organic sealant affixed to the metal surface to be protected, a layer of inert material impregnated with said organic sealant and adhered to the surface of said inner layer of organic sealant, and said sealant with which said material is impregnated being chlorinated at least upon its exposed surface.

15. A corrosion resistant electrolytic cell according to claim 14 wherein the inert material is selected from the group consisting of crocidolite asbestos fibers, synthetic polyester fibers of methyl terephthalate and ethylene glycol and fibers of a copolymer of vinyl chloride and acrylonitrile.

No references cited.

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