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CATHODIC PROTECTION OF METAL CONTAINERS FOR LIQUIDS

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Fig. 1.

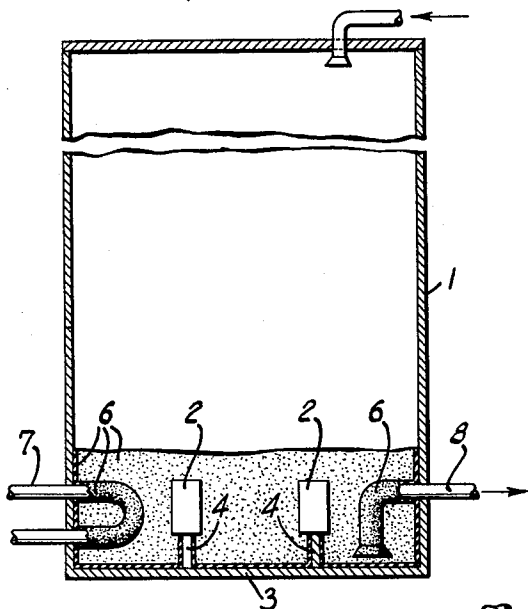


Fig. 3.

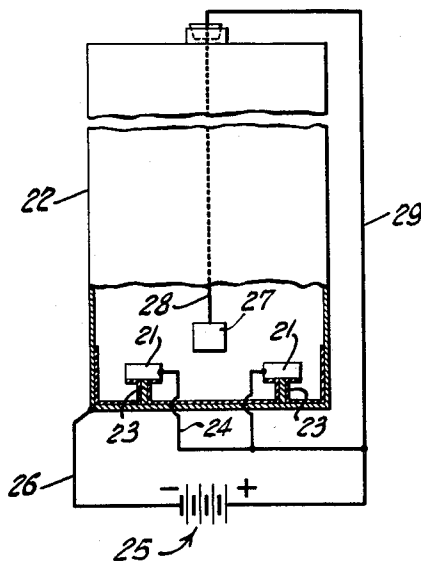
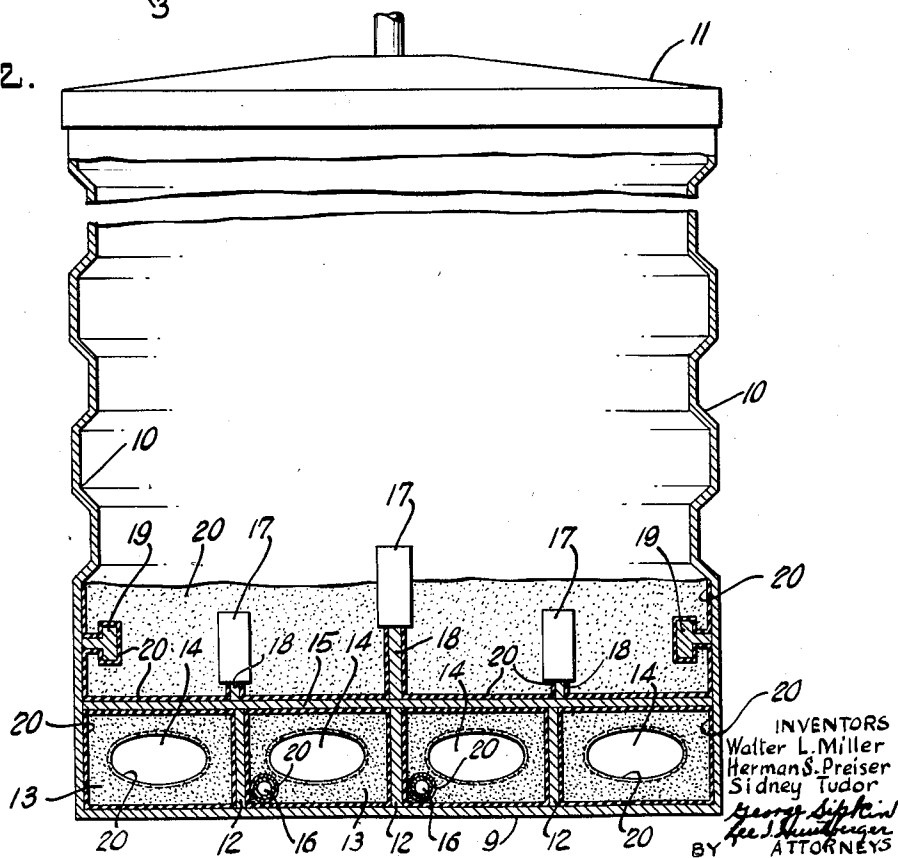


Fig. 2.



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CATHODIC PROTECTION OF METAL CONTAINERS FOR LIQUIDS

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to the cathodic protection of relatively large metal containers or tanks, for liquids to resist corrosion thereof due in part to galvanic currents created in the container or tank when liquids are placed therein. This corrosion protection is accomplished by placing in the metallic tank either at least one sacrificial galvanic anode, such as of magnesium, or at least one relatively inert anode activated by an impressed current. Cathodic protection of this type is very important for cargo tanks that are often used as ballast tanks on tanker ships, as well as for other relatively large tanks or containers of water and other liquids. Cargo tanks of tanker ships are normally filled with water for ballast for only a portion of their total time, and they cannot be cathodically protected while empty or while carrying non-aqueous cargo.

While corrosion and cargo contamination of tanks of tanker ships can be restricted by coating all of the interior walls and other exposed metal surfaces in a tank, with a protective, continuous coating that is resistant to both salt water and hydrocarbon cargos, this is relatively expensive, costing normally from one to two dollars per square foot of surface. A combination of an inert, corrosion resistant coating covering all bare surface in contact with water in conjunction with cathodic protection has been proposed for preserving relatively small and smooth sided tanks such as domestic hot water tanks. In such tanks the cathodic protective current is very small and is used to prevent corrosion of minor areas, such as openings or imperfections in the coating.

In relatively large tanks, such as ship cargo tanks, the most common and most economical method of corrosion protection is the cathodic protection system normally provided by sacrificial anodes of magnesium metal. Such systems are designed to protect all or nearly all of the steel of the tank structure. Single, large, centrally located anodes on the bottoms within these large tanks were found to provide an excessive protective current to nearby surface areas and inadequate protective current to areas of the tank surface that are relatively distant from the anodes. Adequate cathodic protection for large tanks required a multiplicity of anodes well distributed over all of the tank wall areas. In some of such tanks small dielectric shields were used to prevent wastage of current through the short paths to nearby metal surface areas, but they were only partially successful in achieving uniform current distribution. As a consequence uniform, adequate protection without waste of cathodic material was not achieved.

The distribution of such anodes in large tanks presented difficulty in installing anodes and replacing worn anodes. In addition, there was always the hazard of falling anodes. Anodic metals, such as aluminum and magnesium, are

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both known to produce hot sparks upon striking a clean steel surface in the presence of a small amount of iron oxide rust, which action is known as a Thermit reaction. Under proper conditions it can occur with an impact produced by an anode fall of two or more feet. While sacrificial anodes may be securely attached initially, they tend to be consumed more rapidly at areas adjacent to their metal supports, and if this deterioration is allowed to continue to near depletion, the worn anodes are easily dislodged and may fall.

This hazard is now recognized, and while not eliminated it is alleviated by replacement of anodes while considerable anode metal remains. Substitution of inert anodes will not eliminate the hazard because they may be dislodged by vibration or agitation and in themselves may cause sparks upon striking either tank surfaces or a relatively weak structure such as a steam heating coil which then in turn may, in moving, cause sparks by striking the steel bottom or other wall. Aside from mechanical damage caused by falling anode material, resultant sparks in tanks recently emptied of inflammable cargos are liable to produce disastrous explosions.

It is recognized that when liquid cargo tanks are empty or carrying cargo, they normally contain small amounts of water on their bottoms, which results, in the absence of protection, in a severe corrosive action commonly called bottom pitting.

An object of this invention is to provide an improved method of and construction for providing cathodic protection of metallic containers for liquids against the corrosion and damage due in part to galvanic currents in said container in contact with the liquids therein, which will avoid dangers of explosions and damage due to falling anodes, which will be exceptionally effective and durable in the protection, easily practiced, and relatively simple and inexpensive to practice.

Another object is to provide protection to a container for liquids which will have adequate resistance to damage due to corrosion and pitting in the container when partially filled with liquids not in contact with said at least one anode, which will have adequate permanence and effectiveness, which will be resistant to different liquids placed in the container, and which will be relatively simple, practical, durable and inexpensive in construction.

A further object is to provide for the protection of tanks of cargo ships or tankers that may be filled with sea water or liquid cargo as occasion may require, which provides greater protection than is possible by cathodic protection alone and at lower cost, which will require little or no servicing attention for relatively long periods, which may be provided in a container without the necessity of erecting staging and without difficult working conditions, and which will give adequate protection with a minimum amount of anodic material and at relatively low cost.

Other objects and advantages will appear from the following description of an example of the invention and the novel features will be particularly pointed out hereinafter in connection with the appended claims.

In the accompanying drawing:

Fig. 1 is a schematic sectional view of a metal tank of general utility illustrating one manner in which cathodic protection therefore may be provided in accordance with this invention;

Fig. 2 illustrates schematically a cross section of a simple example of a ship's cargo tank also provided with cathodic protection in accordance with this invention; and

Fig. 3 is a schematic circuit diagram illustrating the manner in which an impressed voltage may be applied when using relatively inert anodes, and also illustrating another manner of mounting anodes of any type in a tank.

In the example of the invention illustrated in Fig. 1, as applied to any metallic, liquid storage tank 1, such as an industrial storage tank, one or more relatively large bodies 2 of sacrificial anodic material, such as of magnesium, zinc, aluminum, and suitable alloys are mounted in the interior of a tank to be protected, preferably near but above and spaced from the bottom 3 of the tank, and in electrical connection with the tank. Such anodic bodies 2 are mounted within the lower part of the tank on metallic members 4 upstanding from the bottom 3 of the tank, or to any stiffening or reinforcing members of the tank, or upon any convenient projecting structure of the tank, through which anodes are electrically connected to the tank structure. Preferably the anodic body or bodies 2 should be spaced well from the sides of the tank.

A substantially water impervious and continuous coating 6 of a dielectric insulating material that is resistant to deterioration by galvanic currents, water and any other liquid that may be placed in the tank, such as liquid petroleum products for example, is applied to exposed metal surfaces within the bottom portion of the tank, including the floor and any heating and other pipes 7 and 8 and any metal braces, stiffening members and metallic projections that are closely adjacent to the anode surfaces or to the floor of the tank. This coating is substantially continuous beneath and in proximity to the anodes and for a substantial distance horizontally therefrom, and it preferably covers the entire floor and up the exposed sides of the tank for a substantial distance, but not exceeding about 50% of the full height of the side walls. For example, the coating may advantageously extend up the sides of the tank from the floor thereof for a distance conveniently reached by a person while standing on the tank bottom structure, which would usually be for a distance from about four to six feet above the part of the tank bottom structure on which the person may be standing. No temporary scaffolding or staging is required. When the side walls are coated part way up, preferably all exposed surfaces of metal structures within the tank below the upper level of the coating on the tank side walls are covered with the dielectric coating material.

It is recognized that the longer an electrolytic path, the more uniform is the galvanic current distribution, and in accordance with this invention, there is a relatively long path from the anodic bodies 2 to the nearest exposed metal surface of any part of the tank or metallic members or projections within the tank. The minimum length of such current paths will depend somewhat upon the size of the tank. The minimum length should be large enough to generally equalize the resistance of the current paths in all directions from the anodic material to the exposed metal of the tank that may be in contact with an aqueous liquid held in the tank, but it will be obvious that all of the possible current paths cannot be closely equalized, nor is it necessary. It has been determined from actual measurements that the resistance of a current path increases logarithmically with distance between anode and cathode. The resistance value changes very slowly, almost negligibly as the anode to cathode distance varies above 50 anode diameters, where the anode diameter is defined as the diameter of a circle whose area is equal to the cross-sectional area of the anode in question.

It has been found experimentally that major changes in the resistance path of the liquid occur within about the first ten said anode diameters distance between the anode and the cathode, after which the changes are relatively small. Therefore, for purposes of this invention the minimum anode to cathode distance should be in the order of about 10 said anode diameters measured as the shortest path between the nearest edge of the anode and the bare metallic container cathode. For example, it would not be advisable to locate an anode of 6" equivalent diameter within a minimum of about five feet of

any exposed metal in the cargo tanks of an average sized tanker ship and a greater distance would be advisable. In smaller tanks, where a smaller anode may be used, this minimum distance may be reduced proportionally. This is particularly suited to give adequate uniformity in the galvanic current distribution, and hence maximum protection to the tank, especially when the tank is filled with sea water.

Where the tank is rather wide or broad and the anodes 2 are arranged near the central area of the tank bottom, one can obtain a relatively long path for travel of a galvanic current from the anodes to the nearest exposed metal of the tank when the coating on the bottom wall of the tank terminates somewhat short of the side walls and does not extend up the side walls of the tank. Some beneficial results may be obtained under such conditions. However, to be certain that adequate cathodic protection is provided under all conditions, it is preferable to extend the protective coating close to, or entirely to the side walls, and also up the side walls to the extent explained hereinabove. When the tank is empty or carrying cargo there is a tendency to severe pitting at the bottom of the tank from small amounts of water that enter in various ways, or which remain when the tank is emptied of water. The bottom coating protects against this type of corrosion.

When the tank is filled with water, particularly sea water, the coating 6 serves as an insulator to prevent excessive wastage of protective current to nearby exposed metal of the tank, and automatically causes the protective current to be distributed with relative uniformity to all uncoated parts of the tank. The coating of the bottom of the tank, the lower metal parts in the tank and the sides of the tank near the bottom serves also to prevent corrosion of those parts while the tank is relatively empty or carrying non-aqueous cargo. The anodes are located to give generous spacing without placing them in close proximity to the tank walls. The tank dimensions must be considered in this respect.

In applications of this invention to tanks that may ever be expected to carry combustible or inflammable cargos, the coatings 6 and 20 should be thick and tough enough to resist or prevent penetration thereof by falling anode material in the tank, and also soft and resilient enough to avoid the creation of sparks if struck by such falling anode material. A suitable coating material for the tank bottom, sides and exposed metal surfaces, is "Tarsel" made by Pittsburgh Coke and Chemical Company and which is a coal tar modified, amine cured, epoxy type of resinous paint. The epoxy type of resin is one formed by a combination of bisphenol and epichlorohydrin, modified, when desired, by another material such as coal tar, and hardened by reaction with an amine, such as diethylene triamine, for example. Another suitable hardener for the resin is available in the trade under the name "Versamid 125" made by General Mills, Inc., and which is a fatty acid converted to a long chain amide. The resin may be thinned, when necessary or desirable, by a suitable solvent to facilitate its application to the metal surface. There are a number of variations of the epoxy and ethoxyline type resins available in the market and all of them appear to be particularly useful for coatings in accordance with this invention. Disclosures of a substantial number of such resins are given in U.S. Patents #2,691,007, #2,324,483, #2,444,333, #2,494,295, #2,500,600, #2,739,134 and #2,511,913, and in British Patents #518,057 and #579,698 to which reference is made for more information as to such resins. These epoxy and ethoxyline resins are particularly useful as the coatings 6 and 20 because they can form dielectric films or coatings of any desired thickness that are sufficiently soft, resilient and tough to resist and prevent penetration thereof, and formation of sparks by anodic material falling thereon. Another type of coating that may be

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used is zinc silicate or a cementitious material such as Portland cement mixed with an added silicate to make the coating impervious to liquids.

Additional resinous coating materials that may be used are the isocyanate resins, and the aldehyde condensation type of resins of either the cold cured or the hot set type. A useful coating in the absence of organic solvents in the tanks may comprise dielectric materials having elastomeric properties, such as tar, latex, synthetic rubber, asphalt, and mixtures thereof. Other coating materials may be used if they have the desired properties of being dielectric, soft, tough and resilient, and resistant to galvanic currents, water and other liquids that may be placed in the tank to be protected. For use in tanker ships, the coating should also be resistant to organic liquid cargos as well as salt water.

Referring next to the example of the invention illustrated in Fig. 2, the tank protected is shown schematically as a tank or holder such as may be found in a typical cargo or petroleum tanker ship. It has a bottom wall 9, side walls 10, a top 11, spaced ribs 12 upstanding from the bottom, braced by spaced apart cross plates 13 with apertures 14, and cross bars 15, all of metal. Pipes 16 extend above the bottom between the ribs 12 and pass through apertures in the cross plates 13. The anodes 17 are mounted on the ribs 12 and bars 15 by short metal uprights 18 that provide electrical connection from the anodes to the tank walls. The central anode 17 may be, if desired, disposed or extended slightly higher than the anodes nearer the side walls. The side walls of the tank may have stiffening strips 19 along the sides near but above the bottom wall 9 of the tank. A coating 20, similar to coating 6 of Fig. 1, is applied to the exposed upper surface of the bottom wall 9, the exposed surfaces of the stiffening and bracing members 12, 13, 15 and 19, the piping 16, the anode supports 18 where exposed in the lower part of the tank, and also preferably the inner exposed sides 10 of the tank for a short distance up from the bottom, as explained in connection with tank 1 of Fig. 1.

Where the tank of Fig. 2 is broad in horizontal dimensions and the anodes are space well from the sides of the tank, the bottom wall is coated in the areas beneath the anodes and horizontally therefrom for an area against which the anode may fall, and approaching the side walls at least for enough to provide a path of minimum length of ten said anode diameters from the anodes to the exposed metal surfaces within the lower part of the tank, but in such cases the coating may not reach the margins of the bottom wall or extend up the sides. However, the coating preferably extends over substantially all of the bottom and up the side walls and over the metal parts in the lower part of the tank as explained for Fig. 1.

It is possible to use for protection, in all embodiments of the invention, non-sacrificial or relatively inert anodes 2 or 17, when a small, impressed, direct current voltage is applied between the anodes and the metal of the tank. In such cases the anodes may, for example, be of metallic lead, high-silicon iron, platinum or graphite, and the impressed current may be obtained from a generator, batteries or a rectifier. While any impressed voltage may be applied, it is advisable to use only small voltages of about 2 to 6 volts for safety and economical reasons. A dielectric coating 6 or 20 should be applied as explained hereinabove for Figs. 1 and 2. This is illustrated schematically in Fig. 3 in which relatively inert anodes 21 are mounted in any suitable manner in the tank 22 but insulated from the tank by their supports 23. The anodes are electrically connected by insulated conductors 24 to the positive side of a battery 25 or other source of low D.C. voltage, the negative side of the battery being connected by conductor 26 to the metal of the tank.

In some instances, particularly in stationary tanks, it may be desirable to support an anode from the top of

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the tank, but with the anode in proximity to the bottom, which makes it easy to remove the anode from the tank for inspection or replacement. This is also illustrated in Fig. 3 in which an anode 27 is suspended by a conductor 28 from the top of the tank 22. The conductor 28 should be covered with an insulating coating, or provided with such a coating at the time of its manufacture. The conductor 28 is electrically connected to the anode 27, and if this anode is of the sacrificial type the conductor 28 will be connected to the tank. If the anode is of the relatively inert type, then the conductor 28 should be connected by a wire 29 to the positive side of the impressed voltage from D.C. source or battery 25. The suspended anodes 27 may be used alone or in conjunction with the anodes 21 that are supported from the bottom of the tank.

The present cost of providing cathodic protection in an average tank of a T-2 type tanker ship is about \$2,500 where numerous magnesium anodes are placed all around in the tank. Replacement costs of about \$1,000 are necessary about every two years so that at the end of twelve years, the total cost is about \$7,500. With the arrangement of anodes and coating in accordance with this invention, cathodic protection for twelve years will cost about \$5,200 for the same size tank, in which the initial installation cost is about \$4,000, with anode replacement and paint repairs at four year intervals costing about \$600 each. This lower cost for a long range installation in accordance with this invention is possible because in the case of a ship tank, all of the installation work is performed at the bottom of the tank without the use of any erected staging or scaffolding and without difficult working conditions. Furthermore, in order to protect an unpainted area of about 70% of the tank, 70% or less of the magnesium is required and this may be concentrated in larger, more economical sizes such as 70 lb. magnesium anodes instead of the more commonly used 50 lb. magnesium anodes. When the larger anodes are used, fewer need be installed.

The service life of the anodes is approximately doubled in accordance with this invention because of the saving of the large amount of current wasted at low resistance cathode areas near the anodes. The size and amount of galvanic anodes will vary for each tank geometry and internal surface area, but generally sufficient anode area and weight are provided to produce a total current output in the range of about 3 to 10 milliamperes per square foot of exposed cathodic tank surface for about a two year period. For intermittent usage such as salt water ballasting cargo oil tanks of tankers, the galvanic anodes will last about twice as long. For impressed current inert anodes, the size and shape of the anode is determined by the current output required and the driving voltage specified.

While the invention has been described as used in connection with tanks of ships and other tanks into which heating pipes extend as examples of use of the invention, the same protection is useful for, and may be advantageously employed with, any large metal tanks for continuous or intermittent storing or transporting of water, or other corrosive liquids. The heating pipe could be omitted when no heating of the contents of the tank is desired.

This application is a continuation-in-part of our co-pending application Serial No. 697,504, filed November 19, 1957.

It will also be understood that various changes in the details, steps, materials and arrangements of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

We claim:

1. A metallic holder for liquids having uniform, efficient cathodic protection against corrosion, by any liq-

uids contained therein, of its exposed interior surfaces, which comprises a metallic enclosure for said liquids of the size of cargo tanks of ships, and having electrolytic anodic material supported by said enclosure within it and spaced somewhat above but in proximity to the floor of the enclosure or any projecting structure just above the floor, said enclosure having material on that portion of its floor and any said projecting structure which lies beneath said anodic material and horizontally therefrom over any area upon which any of said anodic material might fall if dislodged from its support, a coating of a dielectric material that is inert and impervious to any liquids likely to be placed in said enclosure and which when struck by any metal falling through a distance equal to the depth of the enclosure will not create sparks and leaving at least 40% of the inner surface of the enclosure uncoated and exposed to said liquids that may be placed in said enclosure, and circuitry connecting said anodic material and said enclosure to form therewith an electrochemical cell when any liquid placed in said enclosure functions as an electrolyte.

2. The holder as set forth in claim 1, wherein the minimum direct distance between said anodic material and the nearest uncoated, exposed metal surface within said enclosure is at least about ten anode diameters where an anode diameter is defined as the diameter of a circle having an area equal to the cross-sectional area of a body of said anodic material within the enclosure, said minimum distance representing the minimum length of current path between said anodic material and the exposed uncoated metal of said enclosure required for substantially uniform current distribution between said anodic material and the metal of said enclosure through the liquid contained within the enclosure.

3. The holder as set forth in claim 1, wherein said coating covers substantially the entire floor of said enclosure and any of the projecting metallic structure of the enclosure which is attached to said floor and lies below the highest level of any of said anodic material.

4. The holder as set forth in claim 1, wherein said coating also extends up the side walls of the enclosure from the floor for a minor part of the height of such side walls, the balance of the side walls being substantially and directly exposed to any liquid filling the enclosure.

5. The holder as set forth in claim 1, wherein said coating has a thickness and strength adequate to prevent its penetration by any of said anodic material which may fall thereon.

6. The holder as set forth in claim 1, wherein said anodic material is in the form of at least one anode body, and its support by the enclosure is through a metal member that electrically connects the body and enclosure.

7. The holder as set forth in claim 1, wherein said coating is basically composed of an amine cured, epoxy type of resin.

8. The holder as set forth in claim 1, wherein said coating is basically composed of a long chain amide cured, epoxy type of resin.

9. The holder as set forth in claim 1, wherein said coating is largely zinc silicate.

10. The holder as set forth in claim 1, wherein said coating comprises an isocyanate resin.

11. The holder as set forth in claim 1, wherein said coating comprises an aldehyde condensation type of resin.

12. The holder as set forth in claim 1, wherein said coating contains a substantial amount of coal tar.

13. The holder as set forth in claim 1, wherein said coating has elastomeric properties.

14. The holder as set forth in claim 1, wherein said anodic material is of the sacrificial type.

15. The holder as set forth in claim 1, wherein said anodic material includes an anode body carried by the upper part of said enclosure by an insulated, electrically conductive element.

16. Holders as set forth in claim 1, wherein said anodic material in each enclosure is in the form of at least one body and said bodies are selected in size, number and positions in an enclosure to produce in each enclosure a total concurrent galvanic current output in the range of about three to ten milliamperes per square foot of exposed, uncoated metal surfaces within said enclosure.

17. A holder as set forth in claim 1, wherein said anodic material is activated by a driving voltage sufficient to produce a current of about three to ten milliamperes per square foot of exposed, uncoated metal surfaces within said enclosure.

18. A metallic holder for liquids having uniform, efficient, cathodic protection against corrosion, by any liquids contained therein, of its exposed interior surfaces, which comprises a metallic enclosure for said liquids having a size at least as large as cargo tanks of ships, electrolytic anodic material supported within and by said enclosure and spaced somewhat above but in proximity to the floor of the enclosure and of any projecting structure just above said floor on an interior face of said enclosure, said enclosure having a continuous soft coating of a dielectric material solely on that part of the inside face of said enclosure on that portion of its floor and any of said projecting structure which lies beneath said anodic material, and horizontally from said anodic material over any area upon which said anodic material might fall if it became released from the part of the enclosure to which it was attached for support and for a distance from said anodic material adequate to cause substantially uniform current distribution between said anodic material and any uncoated exposed metal of the enclosure through any liquid contained within said enclosure, said coating material being impervious and inert to any liquid likely to be placed in the enclosure, and covering less than about 60% of the interior wall surface of the enclosure, the balance of such interior wall surface being uncoated and exposed to direct contact with the contents of the enclosure.

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