

Nov. 21, 1967

G. T. SHUTT
METHOD AND SYSTEM FOR PROTECTING CORROSIBLE
METALLIC STRUCTURES

3,354,063

Filed May 9, 1966

4 Sheets-Sheet 1

FIG. 1.

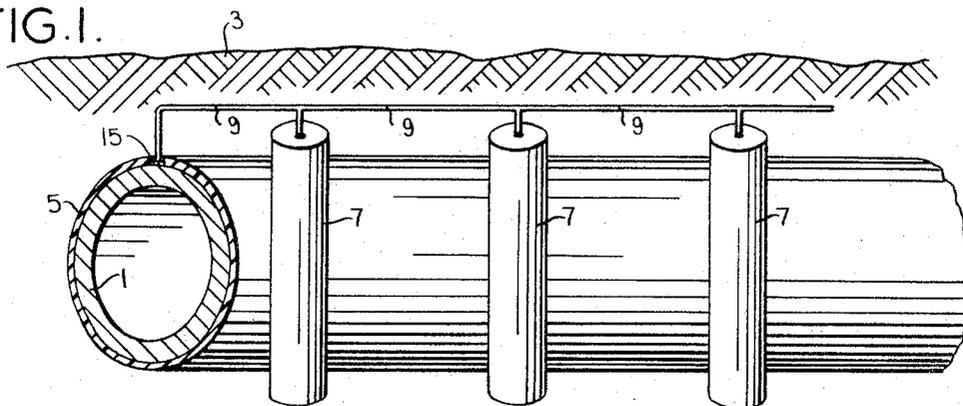


FIG. 2.

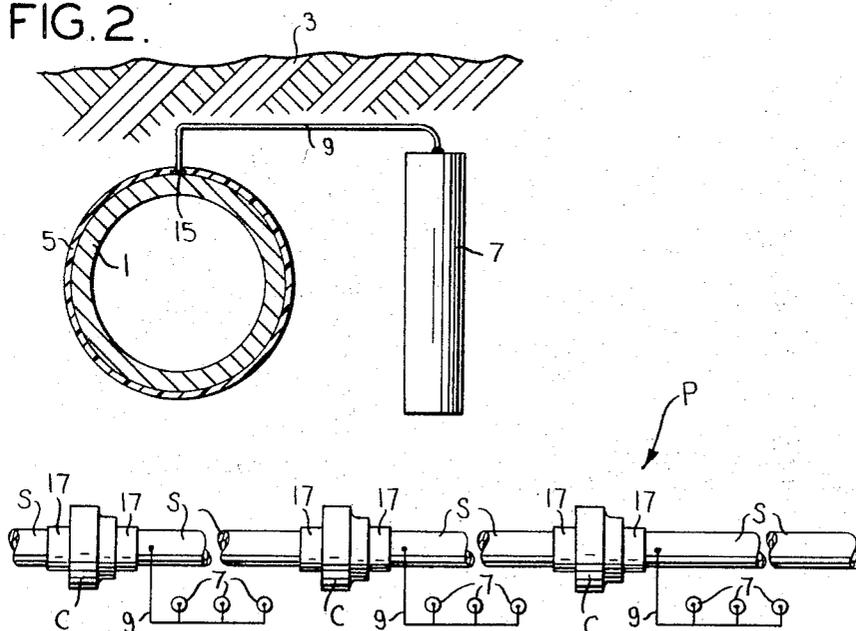


FIG. 3.

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FIG. 4.

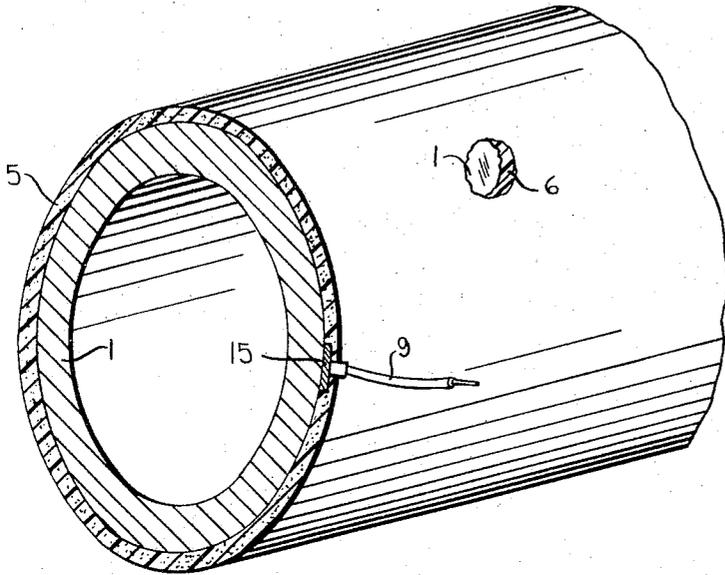


FIG. 5.

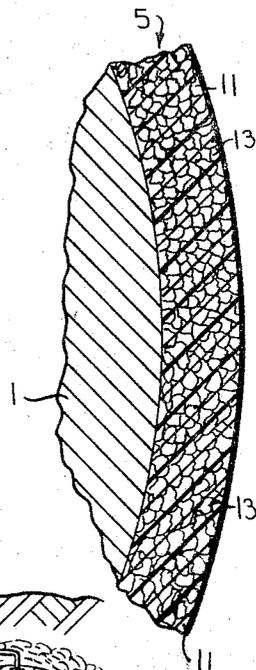


FIG. 6.

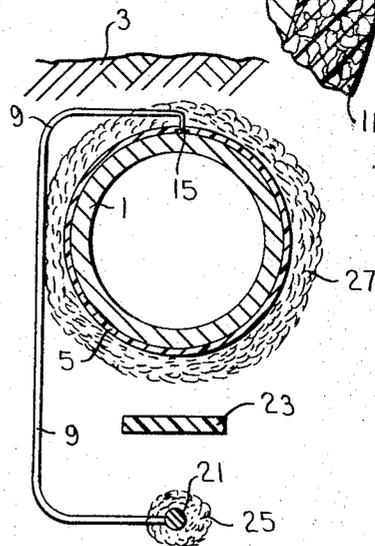
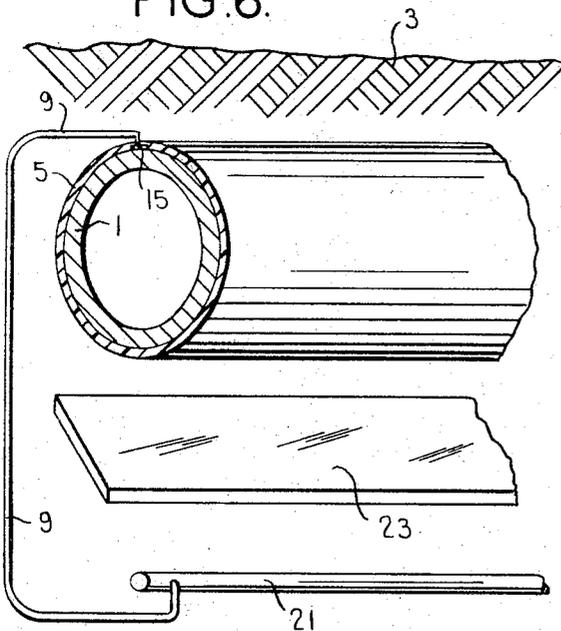


FIG. 7.

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FIG. 8.

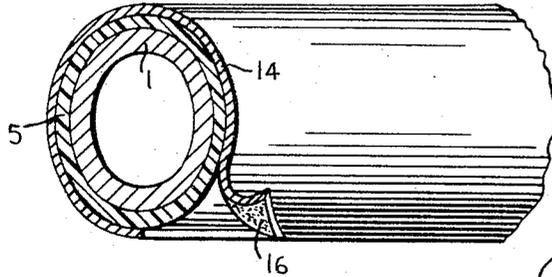


FIG. 9.

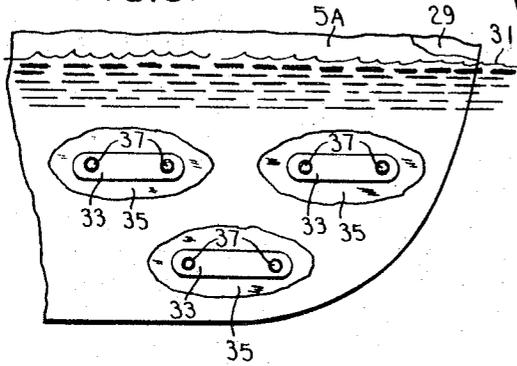


FIG. 10.

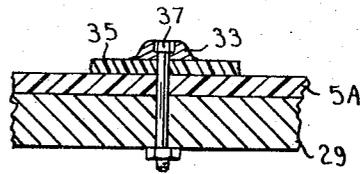
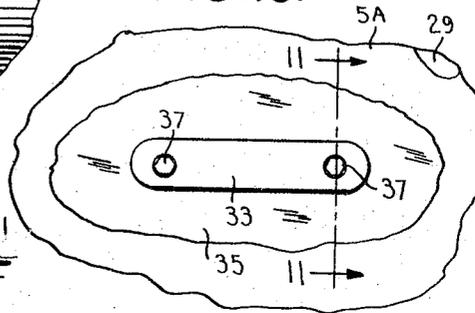
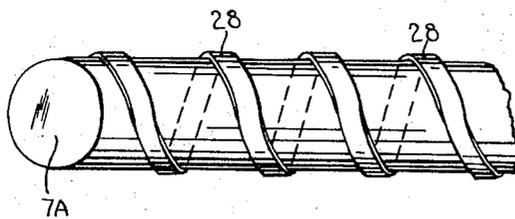


FIG. 11.

FIG. 12.



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FIG. 13.

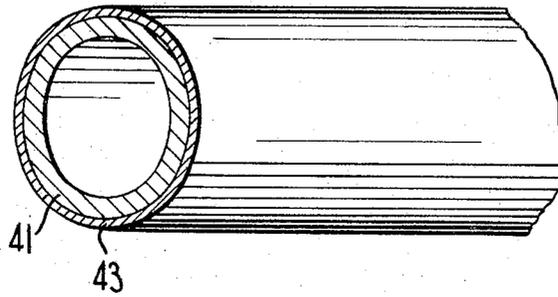
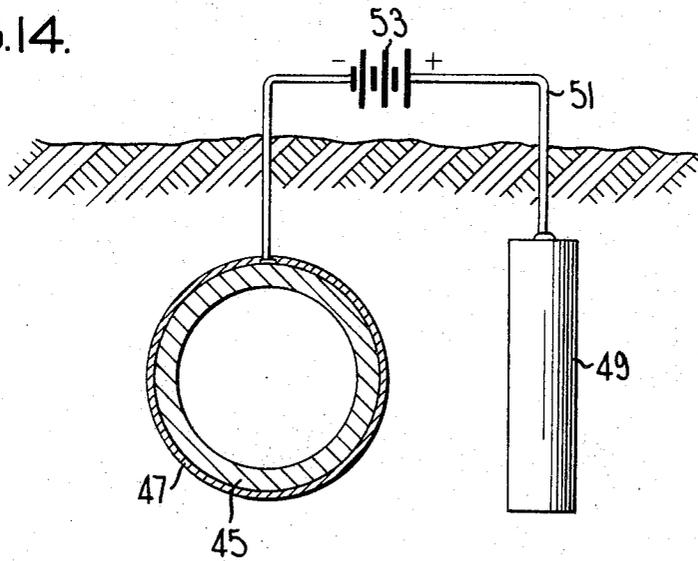


FIG. 14.



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2

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METHOD AND SYSTEM FOR PROTECTING CORROSIBLE METALLIC STRUCTURES

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 Filed May 9, 1966, Ser. No. 548,675
 38 Claims. (Cl. 204-148)

This application is a continuation-in-part of my copending patent application Ser. No. 386,173, filed July 30, 1964, now abandoned, entitled, System for Protecting Corrosible Metallic Structures, and my copending patent application Ser. No. 458,823, filed May 12, 1965, now abandoned, entitled, System for Protecting Corrosible Metallic Structures.

This invention relates to a system for protecting corrosible metallic structures, and more particularly to cathodic-anodic corrosion control of underground, submerged or embedded metallic structures, such as pipes, storage tanks, ships' hulls, off-shore drilling rigs, ground rods, reinforcing rods in concrete, anchor rods, etc.

Typical prior art cathodic protection systems are generally of two types. In one type, anodes of magnesium or the like are placed in the ground near a steel structure to be protected and are connected by an insulated conductor to the structure and a current flows through the soil from the anode to the structure due to differences in solution or corrosion potentials of the anode and structure, these potentials being selected so that current flows onto the structure being protected to make it cathodic and prevent corrosion. The other general type of cathodic protection available utilizes an electrical conductor in the soil, the structure to be protected and the conductor being connected to an external source of D.C. voltage, the polarity of the voltage being such that the structure to be protected is maintained cathodic. These systems both require large current flow for adequate protection. Conventionally, insulating coatings are applied to the structure to be protected to attempt to reduce this current flow.

Cathodic protection systems of the types described are affected by other nearby cathodic systems due to large current flow and may also be affected by lightning and nearby high voltage transmission lines. In a typical prior art pipe protection system a thick (10-600 mils) non-conductive coating for isolating the pipeline from the electrolyte is applied to the pipeline near the jobsite or "over the ditch," and great care must be taken to prevent cuts or breaks (so-called "holidays") through the coating where localized corrosion can take place. Such coatings having short storage life are subject to attack by vermin, bacteria, solvents, etc., and limit bending of the coated pipe. Furthermore, with these systems boring (such as under highways and the like) cannot be accomplished by use of the pipe itself due to the coating thereon and it is necessary to use a separate bore pipe to make the hole, then remove the bore pipe and insert the coated pipe. Generally speaking such prior art systems are considered to be only about 70% effective in protecting a corrosible structure.

Accordingly, among the several objects of this invention may be noted the provision of an improved method and means for protection of corrosible structures with or without a power supply; the provision of such a system wherein the structure can be coated in the shop and has a long storage life, and wherein the coating applied is substantially immune from attack by vermin, bacteria, solvents, etc. encountered in a corrosive soil; the provision of a protection system for corrosible structures in which the structure can be handled immediately after application of a coating of the system to the structure; the provision of

a method and system for protecting a corrosible structure in which the passivity or inertness of the structure in an electrolyte can be controlled; the provision of a protection method and system for corrosible structures using a protective electrode with an extended useful life, and the provision of such a method and system in which the activity of the electrode can be controlled; the provision of a pipe protection system which will not interfere with other nearby cathodic protection systems nor be affected by lightning or high voltage transmission lines; the provision of a pipe protection system wherein thin coatings are used without loss of adequate protection of the corrosible structure, and wherein the coated structure can be bent to small radii without impairing the effectiveness of the coating; the provision of pipe protection systems wherein the pipe to be protected may be used for boring; the provision of a pipe protection system wherein substantially 100% protection can be obtained; the provision of an improved method and system for protecting corrosible structures which includes both cathodic and anodic corrosion control; and the provision of a system for protecting corrosible structures in water, concrete, or other liquid or solid electrolytes. Other objects and features will be in part apparent and in part pointed out hereinafter.

The invention accordingly comprises the constructions and methods hereinafter described, the scope of the invention being indicated in the following claims.

In the accompanying drawings, in which several of various possible embodiments of the invention are illustrated,

FIG. 1 is a side view, partially broken away, illustrating a system of this invention protecting a pipe;

FIG. 2 is a view from the left end of FIG. 1;

FIG. 3 is a plan view of a plurality of pipeline sections protected by the protection system of this invention;

FIG. 4 is an enlarged fragmentary perspective view of the coated pipe showing an insulated conductor connected to the pipe through the coating;

FIG. 5 is a greatly enlarged partial section through the coating on the pipe;

FIG. 6 is a fragmentary elevation of a modified form of a protection system of the invention;

FIG. 7 is a view from the left end of the FIG. 6 system;

FIG. 8 is a fragmentary perspective of a coated pipe that has been wrapped in accordance with the invention;

FIG. 9 is a fragmentary view showing a system of this invention protecting the hull of a ship;

FIG. 10 is an enlarged fragmentary view showing in detail a portion of the FIG. 9 system;

FIG. 11 is a section taken on line 11-11 of FIG. 10;

FIG. 12 is an enlarged view of an electrode which has been partially masked in accordance with this invention;

FIG. 13 is a fragmentary view showing a system of this invention for protecting a structure without the use of electrodes; and

FIG. 14 is a view showing a system of this invention using a power supply.

Corresponding reference characters indicate corresponding parts throughout the several views of the drawings.

When a corrosible metal, such as a ferrous metal (steel), is placed in an electrolyte such as corrosive soil, the steel corrodes due to electrolytic action unless the steel is properly protected. In a cathodic pipe protection system the pipe being protected is made cathodic relative to protective anodes or electrodes so that the anodes are sacrificed rather than the pipe which is being protected. Generally speaking, for steel in an electrolytic soil there is a minimum permissible corrosion potential of approximately -.85 volt beyond which steel will not corrode. The "corrosion potential" of a metal or alloy is generally the steady

state irreversible potential it assumes under fixed corrosive conditions measured by using a conventional copper-copper sulfate reference electrode and a voltmeter having a minimum resistance of 100,000 ohms per volt. For the purpose of this discussion these voltages are shown negative, indicating that the measurements are pipe-to-soil. Another criterion for preventing corrosion of steel in an electrolytic soil is to obtain and maintain the anodic potential of the steel relative to the soil at least -0.2 to -0.3 volt more negative than the measured (pipe-to-soil) corrosion potential. By maintaining steel pipe at a potential of approximately -0.85 volt (or even more negative) relative to the surrounding soil, or by making its potential at least -0.2 to -0.3 volt more negative than the measured corrosion potential, the pipe will be protected and corrosion of the pipe prevented. The present invention accomplishes this result either with or without the use of external voltage sources.

In one embodiment of the system of the present invention, the minimum desirable corrosion potential is obtained by application of an electrically conductive coating to steel pipe or other structures to be protected and using electrodes or anodes which preferentially sacrifice themselves to the corrosive soil, the coating and electrodes maintaining the pipe cathodic by approximately -0.85 volt measured from the pipe to the surrounding soil or by increasing the negative potential of steel in the electrolyte by -0.2 to -0.3 volt beyond the measured corrosion potential. In another embodiment of the invention electrodes or anodes are not used and anodic type protection is obtained by passivating a coating on the corrosible structure. This protection is also obtained in the first embodiment after the electrodes have been expended. In a further embodiment the structure is protected by a D.C. voltage impressed between the structure and an electrode.

Referring to FIGS. 1-5 of the drawings, an elongate pipe 1 of a ferrous metal is shown in soil 3, the soil constituting a nonmobile corrosive electrolyte due to the presence of moisture and salts in the soil. On pipe 1 is an electrically conductive coating 5 which is anodic relative to the pipe. The solution potential of the coating relative to the soil is greater (more anodic) than the minimum permissible corrosion potential of the pipe 1. This maintains the pipe cathodic relative to the coating by at least 0.2 to 0.3 volt and prevents corrosion of the pipe. The solution potential as used herein is a measure of the surface-to-soil voltage as established by a copper-copper sulfate reference electrode and voltmeter having a resistance of at least 100,000 ohms per volt. It is a function of the electrochemical reaction between the metal and the electrolyte.

The coating may have small breaks or holidays 6 (FIG. 4) through which the steel pipe is exposed to the soil, and the steel is protected for a time from localized corrosive action at these holidays by the anodic coating surrounding the holidays after the electrodes described later have been expended or overpowered by being grounded (shorted) to more cathodic metal, such as a cast iron or copper water system.

By the use of one or more metallic electrodes or anodes 7, which have an electrical resistance relative to the soil which is low compared to that of coating 5, and anodic relative to pipe 1 (the electrodes 7 being coupled to the pipe by an insulated conductor 9), the pipe 1, including holidays 6, is kept cathodic so that it will not corrode. An electrical circuit is completed through the conductor 9 and electrolyte 3 (the soil) with current preferentially flowing from the low resistance electrode to the coated pipe thereby preventing corrosion of the coating or the pipe. Ultimately the electrode 7 may be expended and may be replaced. Even if the electrode is not replaced, holidays in the pipe 1 are cathodically protected for a period of time after electrode 7 is expended as the coating 5 being anodic relative to the pipe will then preferentially

corrode for a period of time. Ultimately the coating will not sacrifice itself further due to passivation of the surface, such passivation occurring after about 10% of the metal in the coating has chemically reacted due to the corrosion action to form a high resistance film which effects anodic protection of the pipe so covered by this coating. When the preferred epoxy coating is used, the electrolytic action will not cause undercutting of the coating at holidays.

As shown in FIG. 5, the coating 5 comprises a binder 11 and a multiplicity of particles 13 of a metal more anodic (higher in the electromotive series) than the metal of the pipe 1. For example, when pipe 1 is steel the particles 13 are preferably zinc. The particles 13 constitute a major portion of the coating 5 and a sufficient number of the particles are in contact with each other throughout the length and circumference of the coating so that the coating is electrically conductive even though it has a relatively high resistance compared to coatings without the binder. For example, a pure zinc coating would have a resistance of about two ohms per unit area while the coating 5 using zinc particles has a typical initial (i.e., prior to passivation) resistance of about 20 ohms for the same unit area. Resistance values for conventional organic coatings may range from about 1,000 to 1,000,000 ohms per square foot as compared to resistances of about 2 to 15 ohms per square foot for epoxy-zinc coatings used in the system of this invention. After passivation the coating resistance will increase to a level comparable to that of some organic coatings, i.e., 2,000 to 3,000 ohms per square foot. Resistances are determined by the use of a conventional instrument for determining coating resistances. Such an instrument is commercially available under the trade designation "Vibroground," which uses an alternating current to measure ohmic resistance without polarization of the surface. Since the particles 13 are more anodic than the pipe 1, the pipe 1 is cathodic relative to the coating. This relation will continue to exist although after passivation of the outer portion of the coating, the protection of the coated pipe is more a result of the high resistance passive film formed.

The binder 11 may be either organic or inorganic. Suitable organic binders include synthetic resins such as polystyrene, chlorinated rubber, epoxies, polyvinyl acetate, polyvinyl butyl, drying oils, and silicones.

Inorganic binders for the coating are obtained by using silicates such as sodium silicate, phosphates, hydrolyzed ethyl silicates and butyl titanate in the coating solutions applied to the pipe, the resulting coating when cured being inorganic.

A specific inorganic coating suitable for use with the protection system of the invention comprises approximately 80-90% by weight of metallic zinc powder homogeneously mixed with sodium silicate, the particles of zinc preferably being sufficiently small to pass through a 360 mesh screen. Optionally approximately 2% by weight of lead oxide or iron oxide of similar particle size may be included to make the coating slightly less anodic than the electrode. An exemplary organic coating is made using substantially the same percentages of zinc and using a heat-, amine-, or polyamide-cured epoxy resin as the binder.

Preferably the steel substrate 1 is prepared for application of the coating by abrasive blasting or other treatment of the surface to obtain a good commercial finish. Removal of loose contaminant by brushing or wiping may be adequate in some cases. The coating is applied by brushing, pouring, dipping or by spraying with conventional spraying apparatus, preferably utilizing a pot spray apparatus having a mechanical agitator for keeping the metal particles in suspension in the carrier or binder. Where the preferred epoxy-zinc coatings are used it is desirable that the uncured resin and metal particle mixture be heated to a temperature of about 100° - 120° F. as it is applied to the substrate.

The coating 5 is applied over the entire surface to be protected (e.g., the entire outer surface of a pipe) and the coatings are normally dried or cured at room temperature. For example, the zinc and polyamide-cured epoxy resin coating referred to before dries tack-free at 70° F. in approximately three hours and is fully cured in approximately 24 hours. The resulting cured coating is hard and resistant to scratching, chipping and the like, making the coated pipe suitable for use in drilling. The coated pipe may be bent at a small radius without significantly affecting the coating.

While the prior art coatings of nonconductive materials are applied in thick coatings (10 to 600 mils) to isolate the structure from the corrosive soil, the coatings of the invention can be very thin (less than one mil) and are normally approximately 1-10 mils in thickness, a thickness of approximately 2-4 mils being suitable for most applications. In the system of the invention (described later) where the structure is protected by the coating (without using electrodes), then the coating is preferably at least 4 mils.

The coated pipe may be wrapped with a suitable covering 14 (FIG. 8), such as kraft paper. The covering may be about 30 pound weight paper having a thickness of about 3 mils. This covering permits immediate handling of the coated pipe without disturbing the uncured coating. The principal function of the thin covering 14 is to temporarily protect and permit immediate handling of the pipe while the coating dries and cures, and it is thus distinguishable from the thick nonconductive coatings of the prior art referred to above which isolate the pipe from the electrolyte. The electrolyte will readily penetrate covering 14, and the covering does not interfere with the electrical properties of the coated pipe. When the covering is applied over a wet coating it may be in two layers, the first being a perforated or lattice type paper which will tend to trap the coating in pockets in the lattice work and the second being a nonperforated paper. This avoids any tendency of the wet coating to squeeze out from under a single nonperforated covering sheet due to tension on the sheet as it is applied to the pipe.

Covering 14 may comprise a carrier for directly applying chemical materials, such as a passivating ionizable compound, to the pipe instead of placing them in the electrolyte as discussed later. The term ionizable compound as used herein is defined as a chemical compound which under the conditions present in the electrolyte and when the coating is acting as an anode, chemically reacts with the metal in the coating to passivate it; i.e., form a film on the outer surface portion of the coating which has high electrical resistance and will not form a more noble (i.e., more cathodic) surface. The solution potential of a passivated coating is preferably less than the solution potential of the associated electrode. The passivating ionizable compounds determine and control the ultimate passivating and blistering characteristics of the coating. Exemplary ionizable chemical compounds are salts containing radicals of chlorides, sulfides, sulfates, phosphates, silicates, cyanates, carbonates, hydroxides, etc. (e.g., sodium silicate). Preferably these compounds react with the metal of the coating in the presence of the electrolyte and while the coating is acting as an anode to form water insoluble compounds of the metal in the coating, such as zinc hydroxides, zinc sulfates, etc. These ionizable chemical compounds may be carried on the inner surface of covering 14 as indicated at 16 in FIG. 8, or they may be impregnated in the covering or applied per se directly to the coating 5 which may then be wrapped with covering 14. Use of a liquid material such as sodium silicate is advantageous since it serves not only as a passivating ionizable chemical compound but also functions in bonding the covering 14 to the coated pipe or structure if the zinc-containing coating is already dried and cured.

The covering is preferably treated with a release agent such as carnauba wax, silicone, or a dusting type of pas-

sivating ionizable compound to avoid any lifting of the uncured coating from the pipe by adhesion of the coating to the covering in the event the covering is moved away from the pipe before curing of the coating is completed.

The presence of the zinc-rich coating on the steel pipe 1 prevents corrosion of pipe 1 since the coating is more basic or anodic than the pipe. Zinc will polarize itself or establish a solution potential of about -0.80 to -1.2 volt under given soil conditions when connected to electrodes of similar solution potentials. This is either more negative than -0.85 volt (the minimum permissible corrosion potential of steel) or is more anodic by 0.2 to 0.3 volt than the steel substrate.

After electrodes 7 have been expended, or in the embodiments described later where the electrodes are not used, the coating will cathodically protect the pipe or other substrate in the corrosive electrolyte for a limited period of time, i.e., about two to three years or for approximately 200-300 ampere days per 1,000 square feet of coating. This cathodic protection continues until the coating passivates to a resistance comparable to organic coatings due to the reaction of the coating metal with the ionizable compounds and/or the chemicals in the soil or other electrolyte. Then the pipe or other substrate is protected to the extent that it is isolated from the corrosive electrolyte by the passivated surface, i.e., by the preferably water insoluble, substantially inert corrosion products of the zinc particles and ionizable compounds which products form a high electrical resistance substantially chemically impervious film which supplies anodic protection to the structure. Thus the passivated coating protects the coated portions of the pipe by isolation from the electrolyte. When electrodes 7 are provided, they are sacrificed to the soil before there is any significant passivating of the coating because they are more anodic than the coating and they have less resistance to flow of electric current to the soil than the coating 5. Also, the activating compounds described later which are preferably used with the electrodes tend to avoid formation and retention or any impervious nonconductive films resulting from reaction of the electrode material with the corrosive soil and/or activating compounds and therefore they remain active relative to the coating, that is, they react more readily with the soil and are thus preferentially sacrificed prior to any significant corrosion of the coating or substrate.

The electrodes 7 are preferably made of a metallic electrical conductor and most preferably they are or contain the same metal as the particles of metal 13 of the coating, that is, the electrodes are zinc for the exemplary coating specifically set forth hereinbefore. The electrodes may be made of bar, sheet or block form and are spaced from the pipe in the soil. When a plurality of electrodes are used they are spaced from each other at intervals in the soil and are located in a plane generally parallel to the axis of the pipe. The electrodes may be installed in the same ditch receiving the pipe and preferably are spaced more than six inches away from the pipe surface. They may be spaced along the length of the pipe approximately 10 to 5000 feet from each other, depending on soil conditions, surface area, etc. The electrodes 7 are usually slightly more anodic than the coating 5 and the electrode-to-soil resistance is less than the coated pipe-to-soil resistance and, as a result, the electrode will be sacrificed first to the soil due to corrosion before there is any significant corrosion or passivation of the coating itself. When a series of electrodes 7 are provided as shown in FIG. 1, the electrodes are interconnected by the insulated conductor 9. The conductor 9 is attached to the pipe 1 to provide a good electrical path between the pipe and the electrolyte. A metallic contact 15 is preferably connected to one end of the insulated conductor 9, and it may be attached to the pipe 1 by welding, such as that marketed under the trademark "Cadwelding," although other means for attaching the contact may be used. The electrodes may also be in-

dividually connected to the pipe by conductors 9, if desired.

The preferential sacrificing of the electrode will take place when the solution potential of the electrode-to-soil is greater than that of the coated pipe-to-soil because there exists a greater driving potential from the electrode to the soil than from the coated pipe to the soil, thereby producing the desired protection, that is, sacrificing of the electrode prior to corrosion or passivation of the coating or the pipe. Also, as the electrode-to-soil resistance is less than the coating-to-soil resistance as specified above, any tendency is avoided for current to flow from the pipe to the electrode during any transitory situation where the coating may be temporarily slightly more anodic than the electrode.

The protection system of the invention is useful for protecting a long pipe line, a fragment of which is shown in FIG. 3. The pipeline is designated P and comprises a plurality of pipeline sections S each of which may consist of a single length of pipe or a plurality of lengths of pipe in end-to-end relation connected together by couplings, flanges, welding or other suitable means. Each of the pipeline sections S comprises a pipe 1 having a coating 5 thereon as described hereinbefore. Spaced in the soil along each of the pipeline sections S are the electrodes 7 connected by the conductors 9 to the associated pipeline section S. The pipeline sections S are shown interconnected end-to-end by insulating pipe connectors or couplers C. The insulating couplers are ordinarily used only for coupling a pipeline section protected according to this invention with an unprotected section of the pipeline. Since each pipeline section S is independently protected by its associated electrodes 7, the pipeline section S can each be of substantially any desired length, e.g., hundreds of miles, and still be effectively protected by the system of the invention.

It has been found that the portion of a pipeline section most susceptible to corrosion in the electrolyte due to a shorted insulator is at the ends of the pipeline sections adjacent the couplers C, and this may result in some localized corrosion of the coated pipes making up the sections. Therefore, the ends of the pipes forming the sections S are preferably coated with a thin layer 17 of a nonconductive material which may be a tape or coating of rubber, synthetic resin, or other insulating materials. The insulation 17 preferably extends about six inches from the coupling C. In practice, insulation 17 is principally used where a section S of the pipeline protected by a system of this invention is connected to a pipeline section S not protected in accordance with the invention. Coatings 17 may also be used where pipes of dissimilar metals (such as a copper conduit intersecting a steel pipe) are joined through dielectric couplings.

An embodiment of the pipe protection system of this invention is illustrated in FIGS. 6 and 7 of the drawings. In this embodiment the plurality of electrodes 7 interconnected by conductor 9 have been replaced by a single elongate electrode 21 shown in the soil 3 beneath the coated pipe 1. Electrode 21 may be in the form of a wire, rod or tape, is generally parallel to the axis of pipe 1, and is substantially the same length as the pipe. The insulated conductor 9 connects the pipe 1 to the electrode 21 and an electrical circuit is completed through the soil. The electrode 21 bears the same relation to the coating 5 in FIGS. 6 and 7 as electrodes 7 in the previous embodiments. That is, the metal of the electrode 21 is preferably the same metal as the particles 13 of the coating 5, and the relation of pipe-to-soil resistance relative to the electrode-to-soil resistance is also the same as that previously described so that the electrode 21 is preferentially sacrificed to the soil during electrolytic action, thereby protecting coating 5 and pipe 1.

The electrode 21 should be physically separated from the pipe 1 so that there is no metallic electrical path directly between the electrode and pipe except through con-

ductor 9. This separation is obtained, for example, by laying the electrode 21 in the ditch and partially filling the ditch before placing the pipeline in the ditch. As an alternative, an elongated strip of insulating material 23 (such as polyethylene) is located between electrode 21 and coated pipe 1 to provide a physical separation therebetween. Electrode 21 is spaced from the coated pipe any desired distance and is preferably approximately 6-12 inches from the adjacent pipe surface. Electrode 21 can be closer to pipe 1 when material 23 is used.

In both embodiments of the invention described above it may be desirable to use so-called activated electrodes. An activated electrode is an electrode which has a solution potential slightly more negative than the solution potential of the coating and will maintain a low electrical resistance to the flow of sacrificial current so that the electrode will be preferentially sacrificed. This may be accomplished by positioning the electrodes 7 or 21 in an activator material 25 (FIG. 7) by means of which the electrode is maintained active relative to the coating. A suitable material 25 is a sulfate or chloride containing material placed as a backfill around the electrodes and may be, for example, calcium sulfate (gypsum), or a combination gypsum-clay backfill which consists of approximately 50% ground gypsum and 50% bentonite clay when the electrodes are zinc. By using these materials the electrode is maintained active relative to the coated pipe. Corrosion products do not build up as an impervious coating on the electrodes as they are sacrificed, hence the electrodes do not become passive even after significant corrosion has occurred, but rather are maintained active.

As an alternative or in addition to use of the material 25, the coated pipe 1 is placed in a backfill of material 27 (FIG. 7) which is used for passivating the coating relative to the electrode. As previously noted, a passivated coating is one in which the solution potential of the coating may be slightly less than the solution potential of the electrode but one in which the electrical resistance to the flow of sacrificial current from the coating is higher than the resistance to the flow of sacrificial current from the electrode. This occurs naturally to some extent as a result of the corrosion products building up as a film on the coating 5. To synthetically produce a passivated coating, the passivating ionizing material 27 may be placed around at least a portion of the coated pipe 1 along substantially its entire length. Material 27 is constituted by the same chemical compounds or materials set forth above in describing application of the passivating ionizable chemical compounds 16 by covering 14. Thus the pipe is positioned in a material for controlling the coating activity relative to the electrode irrespective of the electrolyte environment. A further advantage of the passivating ionizable materials is the control of blistering of the coating due to osmosis.

In some instances electrical shorts are encountered in the ground or soil which tend to corrode uncoated pipes. For example, the presence of a metal in the ground in contact with and more cathodic than the steel pipe, will cause sacrificing of steel of the pipe due to electrolytic action of the soil and results in corrosion of the pipe. With the protection systems of the invention the presence of foreign structures in the ground which are more cathodic than the coated pipe or the electrodes will not immediately cause corrosion of the coated pipe since the low resistance electrodes or anodes will corrode and sacrifice themselves to the electrolyte before the coating passivates or the pipe corrodes. If the short is not corrected, the electrode will ultimately be totally expended and the pipe is then cathodically protected for a limited period of time by the coating 5 which is anodic relative to the pipe. If the short cannot be corrected by removal of the foreign structure causing the short, then ultimately the coating becomes passivated and will protect the pipe where the steel substrate is not exposed (e.g. at holidays) to the

electrolyte. For this type of protection a coating thickness of about 4 mils or somewhat greater is advantageous.

It is desirable that the useful life of the electrodes be extended for as long as possible, particularly when the electrodes are in low resistance electrolytes where they tend to dissipate rapidly. For a given electrolyte, the life of the electrode is determined by the amount of surface area of the electrode exposed to the electrolyte. Thus, exposure of a large surface area results in faster dissipation of the electrode than exposure of a small surface area. Therefore, by reducing the total area of the electrode exposed to the electrolyte, the life of the electrode can be increased. For example, by reducing the exposed electrode surface area by one-half (without reducing the total quantity of electrode material), the electrode life can be approximately doubled. Reduction in the exposed area of the electrode can be accomplished by masking a portion of the electrode with an insulating material or by changing the shape of the electrode so that a smaller surface area is exposed to the electrolyte. For example, FIG. 12 shows an electrode 7A masked by helically wrapping it with insulating tape 28 with adjacent convolutions of the tape being spaced to expose the desired amount of the electrode in a manner similar to a barber pole. The electrode is made in the shape of a sphere when the minimum surface area is to be obtained by the shape of the electrode. Spherical electrodes can also be masked by tape 28.

The rate at which the electrodes are being expended can be measured or determined by routing the insulated conductor 9 out of the ground or soil and periodically measuring the current flow through the conductor, such being an indication of the current flow through the electrolyte which in turn is an indication of the rate of sacrificing of the electrodes.

In every instance in accordance with the present invention, the solution potential of the electrode must be slightly greater than the solution potential of the pipe coating prior to the interconnection of the electrode to the pipe or metallic structure. The coated pipe, when electrically connected to the electrode(s), will manifest a corrosion potential which is slightly less than, but very close to the solution potential of the electrode. Preferably, the difference in the corrosion potential and solution potential will be 50-200 millivolts or less. Thus there is little current flow from the electrode to the coating, and the electrode is sacrificed at a very low rate when compared with prior art systems in which there is no coating on the pipe.

Specific reference has been made above to protection of pipe and other corrosible structures in soil which constitutes a nonmobile electrolyte. The systems of this invention also have utility in protecting the other corrosible structures in other electrolytes. For example, FIGS. 9 and 10 illustrate a segment of a metallic ship's hull designated 29, a portion of which is subject to corrosion due to exposure to water 31, the water constituting an electrolyte. The hull 29 is protected by coating the portion contacted by water 31 with a conductive coating 5a such as the coating 5 previously described, and then affixing a plurality of spaced electrodes 33 of streamlined configuration to the coated hull. There is a nonconductive insulating coating 35 on the hull between the coating 5 and the electrodes 33 which performs the same function as the coatings 17 previously described. Electrodes 33 are thus positioned adjacent but spaced from the hull. Electrodes 33 are connected by a conductor 37 (shown as bolts) to hull 29. Conductors 37 function in the manner previously described in connection with conductor 9. The outer periphery of the coating 35 is preferably at least 6 inches from the periphery of the electrodes. In other respects, the system is essentially the same as that previously described for protection of pipe in soil. Other submersible or sub-

merged structures such as docks or piers, offshore drilling rigs, etc., can be protected in this manner.

Similar corrosion protection can be afforded other corrosible structures. For example, steel can be protected from corrosion in wet concrete (a solid electrolyte). The steel may be reinforcing bars in bridges, roadways or concrete pilings (in soil or water), piping encased in concrete, anchor rods, etc.

While the systems of the invention described above use electrodes which sacrifice themselves to the electrolyte to protect a substrate, in some instances the provision of such electrodes are not necessary. As shown in FIG. 13, a pipe or other substrate 41 may be simply provided with a coating 43 of the type shown at 5 and 5a and previously described. Coating 43 is passivated either by reaction with ions present in electrolytes or by placing the coating in contact with a suitable passivating ionizable compound, such as by use of a back-fill or by coating a covering with the material, as described previously. In this instance protection is effected initially by the coating serving as an active anode thereby building up a high resistance film while providing cathodic protection and after passivation providing anodic protection because of the resulting isolation of the substrate from the corrosive electrolyte. Therefore the coating should be substantially free of holidays or other breaks which, after passivation and if exposed to the electrolyte, would result in localized corrosion at these holidays. Preferably the coating 43 is at least 4 mils thick since such a coating thickness can be applied by commercial techniques and be essentially holiday free.

Another system of the invention is illustrated in FIG. 14 and comprises a substrate such as a pipe 45 having a coating 47 of the type shown at 5, 5a and previously described. The substrate is connected to an electrode 49 by a conductor 51 in the same manner that electrodes 7 are connected to pipe 1. In this embodiment, however, there is a source of D.C. power diagrammatically shown at 53 connected to conductor 51 so that its negative terminal leads to the substrate 45 and its positive terminal leads to the electrode 49. The D.C. power source may be a battery or rectifier, for example. The voltage impressed is preferably approximately -1.10 volts (measured electrode to soil) and preferably the voltage is controlled so that it does not exceed -1.25 volts. Voltages in excess of -1.25 volts may damage the coating 47.

Electrodes 49 are made from graphite, junk iron, duriron, etc. The source of D.C. power 53 maintains the pipe 45 cathodic relative to the electrode 49 and thereby prevents corrosion of the pipe. Ultimately electrodes may become expended and may be replaced. If the electrodes are not replaced after they are expended, then protection continues for a period of time due to the presence of coating 47 because of its passivation as described above.

The relation between the solution potential of the electrode and coating, as set forth above, has been achieved by using the same metal for the particles 13 of the coating as for the electrode 7. This relation may be established by other means. For example, the coating may contain a metal which is the same as the metal of the electrode mixed with particles of another metal or alloyed with another metal to produce a coating slightly more cathodic than the electrode. For example, with zinc electrodes the metal particles of the coating may be zinc mixed with or alloyed with carbon, iron or stainless steel, tin, copper, etc. Also, the desired result can be obtained by mixtures or alloys of metals which do not include the metal of the electrode and which manifest a net solution potential slightly less than the electrode solution potential, such as magnesium and copper, aluminum and tin, aluminum and copper, etc. The metals are selected and mixed in any desired proportion which will provide a solution potential slightly lower than the electrode potential as set forth hereinbefore. Similarly, the electrode may contain alloys or mixtures of metal par-

ticles to provide the desired slightly higher solution potential relative to the solution potential of the coating by means of which very little current flow from the electrode is achieved.

As noted above the controlled passivation resulting from special treatment with the passivating ionizable compounds permit the use of zinc particles in a binder to be used without a protective electrode if the coating is a minimum of about 4 mils thick. The protective or passivating film created in situ will not be undercut by electrolytic action inasmuch as zinc particles are embedded in the binder material of the coating and if exposed these particles themselves chemically react with the ionizable material to form a further film area thus maintaining the integrity of this passivated coating.

While the systems described herein have been directed more specifically to protection of steel pipelines and ships' hulls, it will be apparent to those skilled in the art that other structures corrosible in soil can also be protected by the system of this invention. For example, this system can be used to protect buried containers, storage tanks, metal beams, off-shore drilling rigs, piers, metals in concrete, and other metal objects subject to corrosion in an electrolyte. Also, this system can be used for protecting structures made of metals other than steel, such as aluminum, copper etc. The electrode material (other than that used for electrode 49 in an energized system) specifically described as being zinc may be of any metal or alloy which is higher in the electromotive series than the metal of the structure to be protected. Such electrodes should also be the same metal or one higher in the electromotive series than the metal of the particles of the coating. For example, such electrodes may be made of zinc, magnesium, special alloys such as zinc-aluminum-cadmium, etc. As to coating materials, the metal particles of the coating may be of zinc, aluminum, magnesium, metal alloys, etc., i.e. any material more anodic than the substrate material.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above constructions and methods without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A system for protecting corrosible metallic structures comprising a metallic structure having an electrically conductive coating thereon, said coating including a nonconductive binder and particles of a conductive metal more anodic than the metal of said structure, said coated metallic structure being positioned in an electrolyte, the coating substantially covering the portion of the structure contacted by the electrolyte and reacting with the electrolyte to form in situ a passivating film, and an ionizable compound in addition to any compound which may be present in the electrolyte, said ionizable compound contacting the coating and controlling the passivating characteristics of the coating in the electrolyte.

2. A system as set forth in claim 1 wherein metal particles constitute a major portion of the coating by weight.

3. A system as set forth in claim 1 wherein the ionizable compound is carried on the surface of the coating.

4. A system as set forth in claim 1 wherein the ionizable compound is carried by a covering on the coated structure.

5. A system as set forth in claim 1 wherein the ionizable compound is a backfill adjacent the coated structure.

6. A system for protecting corrosible metallic structures comprising a metallic structure having an electrically conductive coating thereon including a nonconductive binder and particles of a conductive metal more anodic than that of said metallic structure, and at least

one electrically conductive electrode, said coated metallic structure and said electrode being positioned adjacent each other in an electrolyte, the coating substantially covering the portion of the structure contacted by the electrolyte, and an insulated electrical conductor interconnecting said electrode and said metallic structure, said electrode having a solution potential in the electrolyte which is slightly greater than the solution potential of the coating in the electrolyte whereby the electrode is sacrificed before there is any significant corrosion of the coating and the metallic structure.

7. A system for protecting corrosible metallic structures comprising a metallic structure having an electrically conductive coating thereon including a nonconductive binder and particles of a conductive metal more anodic than that of said metallic structure, and at least one electrically conductive electrode, said coated metallic structure and said electrode being positioned adjacent each other in an electrolyte, the coating substantially covering the portion of the structure contacted by the electrolyte, and an insulated electrical conductor interconnecting said electrode and said metallic structure, said electrode comprising the same metal as the particles of metal in the coating but being more anodic than said coating whereby the electrode is sacrificed before there is any significant corrosion of the coating and the metallic structure.

8. A system as set forth in claim 7 wherein the metallic structure is elongate in shape and said electrode is substantially the same length as the structure and is positioned parallel to the structure.

9. A system as set forth in claim 7 in which the electrode is positioned in a material for activating the electrodes relative to the coating.

10. A system as set forth in claim 7 wherein a portion of the electrode surface area is masked with an insulating material, thereby reducing the electrode surface area exposed to the electrolyte and prolonging the life of the electrode.

11. A system as set forth in claim 7 in which an ionizable compound for controlling passivation of the coating contacts the coating, said ionizable compound being in addition to any compound which may be present in said electrolyte.

12. A system as set forth in claim 11 wherein the ionizable compound is carried by a covering on the coating.

13. A system as set forth in claim 7 wherein the coating particles comprise a metal selected from the group consisting of zinc, aluminum and magnesium.

14. A system as set forth in claim 7 wherein the coating binder comprises a synthetic resin.

15. A system as set forth in claim 7 wherein the coating comprises a mixture of zinc particles and an epoxy resin.

16. A system as set forth in claim 15 wherein the coating comprises approximately 80 to 90% by weight of zinc particles, the coating having a thickness in the order of approximately two to four mils.

17. A protection system as set forth in claim 7 wherein the coating binder comprises an inorganic chemical compound.

18. A system for protecting corrosible metallic pipes comprising a ferrous metal pipe positioned in soil, an electrically conductive coating substantially covering the pipe, the coating comprising a nonconductive binder and particles of a conductive metal more anodic than said ferrous metal, the metal particles constituting a major portion of the coating by weight with contact between the particles providing an electrically conductive path, and at least one metallic electrode positioned adjacent but spaced from the pipe in the soil, and an insulated electrical conductor interconnecting said electrode and said pipe, said electrode comprising the same metal as the particles of the metal in the coating but being more

anodic than said coating whereby the electrode is preferentially sacrificed before there is any significant corrosion of the coating.

19. A pipe protection system as set forth in claim 18 wherein the coated pipe is at least partially surrounded by an ionizable compound for controlling the coating activity relative to the electrode.

20. A pipe protection system as set forth in claim 18 wherein the electrode is at least partially surrounded by a compound for activating the electrode relative to the coating.

21. A pipe protection system as set forth in claim 18 wherein the coating particles and the electrode are both zinc.

22. A system for protecting corrosible metallic structures in a liquid electrolyte comprising a corrosible metal structure, at least a portion of the structure being exposed to a liquid electrolyte, an electrically conductive coating substantially covering the portion of structure exposed to the electrolyte, the coating comprising a non-conductive binder and particles of a conductive metal more anodic than that of said metallic structure, the metal particles constituting a major portion of the coating by weight with contact between the particles providing an electrically conductive path, and at least one metallic electrode positioned adjacent but spaced from the structure in the electrolyte, and an electrical conductor interconnecting said electrode and said structure, said electrode comprising the same metal as the particles of the metal in the coating but being more anodic than said coating whereby the electrode is preferentially sacrificed before there is any significant corrosion of the coating and the structure.

23. A protection system as set forth in claim 22 wherein there is a nonconductive insulating coating on a portion of the conductive coating, the insulating coating being positioned between the electrode and the conductive coating.

24. A system for protecting corrosible metallic structures comprising a metallic structure having an electrically conductive coating thereon, said coating including a non-conductive binder and particles of a conductive metal more anodic than the metal of said metallic structure, and at least one electrically conductive electrode, said coated metallic structure and said electrode being positioned adjacent each other in an electrolyte, the coating substantially covering the portion of the structure contacted by the electrolyte, a source of D.C. power, an electrical conductor connecting the positive terminal of the power source to said electrode and connecting the negative terminal of said power source to said metallic structure, said D.C. power source having a potential which is slightly greater than the solution potential of the coating whereby the electrode is sacrificed before there is any significant corrosion of the coating or the metallic structure.

25. A structure which is protected against corrosion in the presence of an electrolyte comprising a metallic substrate having an electrically conductive coating thereon, said coating including a nonconductive binder and particles of a conductive metal more anodic than the metal of said substrate, and an ionizable compound in addition to any compound which may be present in the electrolyte, said ionizable compound contacting the coating and controlling the passivating characteristics of the coating in the electrolyte.

26. A structure as set forth in claim 25 which further includes an exterior covering of an insulating material.

27. A method for protecting corrosible metallic structures comprising the steps of applying on the surface of the metallic structure an electrically conductive coating comprising a nonconductive binder and particles of a conductive metal which is more anodic than the metal of said structure, and placing the coated metallic structure in an electrolyte in the presence of an ionizable compound in addition to any compound which may be present in the

electrolyte and which ionizable compound controls the passivating characteristics of the coating in the electrolyte.

28. A method as set forth in claim 27 wherein an ionizable compound is applied to the coated structure before it is placed in the electrolyte.

29. A method as set forth in claim 27 which further includes connecting by an insulated conductor to said metallic structure an electrode of a metal which is more anodic in the presence of an electrolyte than the metal of said structure.

30. A method as set forth in claim 27 which further includes connecting an electrode to one terminal of a D.C. power source and interconnecting the other terminal of the power source to said structure, placing said electrode in the electrolyte, and impressing a D.C. voltage between the electrode and the structure, said voltage being slightly greater than the solution potential of said coating in the electrolyte.

31. A method for protecting corrosible metallic structures comprising the steps of applying an electrically conductive coating on the metallic structure, said coating comprising a nonconductive binder and particles of a conductive metal more anodic than the metal of the structure, placing the coated metallic structure in an electrolyte, positioning a metallic electrode near the coated structure, the electrode having a solution potential in the electrolyte which is slightly greater than that of the particles of the coating, and electrically connecting the electrode to the metallic structure, the electrode preferentially sacrificing itself before there is any significant corrosion of the coating and the metallic structure.

32. A method for protecting corrosible metallic structures comprising the steps of applying an electrically conductive coating on the metallic structure, said coating comprising a nonconductive binder and particles of a conductive metal more anodic than the metal of the structure, placing the coated metallic structure in an electrolyte, positioning a metallic electrode near the coated structure, the metal of the electrode being the same metal as that of the particles of the coating and said electrode being more anodic than the coating, and electrically connecting the electrode to the metallic structure, the electrode preferentially sacrificing itself before there is any significant corrosion of the coating and the metallic structure.

33. A method for protecting corrosible structures as set forth in claim 32 further including a step of activating the electrode relative to the coating.

34. A method for protecting corrosible structures as set forth in claim 32 further including the step of passivating the coating on the structure.

35. A method as set forth in claim 32 further including the step of contacting the surface of the coated structure with an ionizable compound.

36. A method as set forth in claim 35 wherein the structure is wrapped with a covering immediately after application of the coating.

37. A method for protecting a pipeline constructed of a plurality of corrosible metallic pipes comprising the steps of applying an electrically conductive coating on the metal pipes, said coating comprising a nonconductive binder and particles of conductive metal more anodic than the metal of the pipes, positioning the coated pipes end-to-end in pipeline sections, laying the coated pipeline sections in a corrosive soil, positioning a plurality of metallic electrodes near the pipeline sections with at least one electrode being adjacent each pipeline section, the metal of the electrodes being the same metal as that of the coating particles and said electrodes being more anodic than the coating, and electrically connecting each coated pipeline section to the associated electrodes, the electrodes preferentially sacrificing themselves to the soil before there is any significant corrosion of the coating and the pipe of the sections.

38. A method for protecting a structure at least partially submersible in a liquid electrolyte comprising the

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steps of applying an electrically conductive coating on the portion of the structure subject to corrosion by the electrolyte, said coating comprising a nonconductive binder and particles of conductive metal more anodic than the metal of the structure, positioning a plurality of metallic electrodes adjacent the coated structure, the metal of the electrodes being the same metal as that of the coating particles and said electrodes being more anodic than the coating, and electrically connecting the coated struc-

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ture to the associated electrodes, the electrodes preferentially sacrificing themselves to the electrolyte before there is any significant corrosion of the coating and the structure.

No references cited.

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