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METHOD OF ELECTROCOATING

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Because of the time and labor saving in comparison to other methods, various processes as claimed in U. S. Patent No. 2,200,469 of May 14, 1940, were extensively used during the recent war. One of these uses was for the protection during construction after launching of the under water hull surface of many of the largest ships which were built.

After U. S. Patent No. 2,200,469 was issued, it was found that, without modification, these processes also could be effectively used for the removal of heavy and firmly attached layers of rust from the compartments of gasoline-carrying tank ships. Often these hard and firmly attached rust layers were one-eighth to one-quarter of an inch thick. The utility of these processes is illustrated by the fact that more than 8 tons of rust were removed from one wing tank compartment of a gasoline-carrying "T-2" tank ship having dimensions of approximately 37 x 16 x 40 feet and a surface area of 11,370 square feet. This resulted in a surprisingly large value of more than 1.4 pounds of electrodescaled rust per square foot of surface. In the war zone these de-rusting processes were used for removing tetra-ethyl lead-containing rust layers from gasoline carrying tank ship compartments so that the ships could be used for carrying potable water during part of the European invasion. Because of the comparatively small number of men required for this electrodescaling the resulting savings in man-hours and "dead time" of a tank ship was considerable.

When a protective coating as disclosed in U. S. No. 2,200,469 is deposited on either an old or a new steel marine structure, such as a piling structure, wharf, etc., and is then maintained with an electric current of sufficient density to deposit additional coating in any pores, spalled and flaked areas, or rubbed areas that develop, the structure can be protected for an indefinite number of years. Maintenance currents of one to five milliamperes per square foot of total submerged surface have been found to meet these requirements and give excellent protection to such a structure. Maintenance currents of greater density can also be applied at intervals up to several days between treatments and still obtain excellent protection.

When an electrocoating is formed by one of the methods of U. S. No. 2,200,469 or one of the methods of patent application No. 526,621 of March 15, 1944 (now abandoned) or of patent application No. 9,933 of February 20, 1948 (now Patent Number 2,534,234) on a corrosion-free, non-rusted sur-

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face such as a polished or sand blasted surface the subsequent protective utility of the coating is economically valuable even without frequent renewals.

However, when such an electrocoating is deposited on the surface of a tank ship compartment or tank car compartment which has been descaled by a similar electrodescaling treatment certain difficulties as herein enumerated are later encountered, except when a small maintenance current is used similar to the treatment for piling and the like as above discussed. It is seldom practical or possible to use a maintenance current on the inside of tank ship compartments or tank car compartments, hence an improved process is desirable for this type of operation.

Accordingly the principal object of this invention is to improve the process of electrolytically descaling and electrolytically coating any structural steel surface which can be immersed in or treated by a limited quantity of sea water or a solution containing calcium and magnesium ions in greater or less quantity than sea water.

Another object is to develop an improved primer-type of coating which can be applied to a de-rusted steel surface and which will have useful adhesion and corrosion resistance properties in marine and seriously corrosive industrial atmospheres.

A further object of this invention is to improve the adhesion, bonding, and corrosion resistance properties of protective coatings which are electrolytically deposited from sea water and related solutions in all classes of steel tanks and tank compartments.

Another object is to condition any electrolytically de-rusted steel surface so that a useful long-life corrosion resistant composite or multiple component electrocoating can be firmly bonded thereto.

As previously stated the hard and firmly attached rust layers on the surfaces of a heavily corroded compartment of a tank ship can be efficiently and effectively de-rusted by the methods of U. S. No. 2,200,469 at very low costs in comparison to other present day practice. However, if electrocoatings are then deposited on such a de-rusted surface by a continuation of the sea water electrocoating process, the resulting coatings are not adequately bonded and therefore do not suitably meet the requirements of present day specifications. Repeated full scale tank ship compartment tests supplemented with many small scale panel tests have shown that

the difficulty is due to insufficient adhesion at the coating-metal interface. Such poorly bonded coatings on these electrolytically descaled surfaces soon begin to spall and flake, thereby again exposing the bare metal.

It should be mentioned that a small maintenance current decreases any serious spalling and flaking; however, such an operation, for example, is impractical for gasoline-carrying tank ship compartments which may be in contact many days with either the atmosphere, gasoline or ballast water.

Therefore this invention covers practical and effective methods of bonding to a de-rusted steel surface electrolytic protective coatings of the types produced by U. S. No. 2,200,469 or by either patent application No. 526,621 of March 15, 1944, or No. 9,933 of February 20, 1948.

It should be noted that the use of sea water as a basic electrolyte for these various processes, particularly when treating tank ship compartments, is due to one or more of the following factors: (a) its availability at or near all ports in the world, (b) its extreme constancy of composition in the various oceans of the world, (c) its low cost, for example, merely the pump cost on tank ships, (d) its convenience in use by avoiding the expense and complication of the labor and equipment required to mix large quantities of individual chemical compounds to give a suitable electrolyte for treating a tank ship compartment, and (e) as herein discussed the efficacy of the results in comparison to other electrolytes.

For simplicity of description, an "electrocoating" will be defined herein as a non-metallic protective coating of two or more components which has definite corrosion inhibiting properties and which is electrolytically deposited from a solution containing magnesium and calcium ions as disclosed in patent applications No. 526,621 of March 15, 1944, or No. 9,933 of February 20, 1948, or from sea and sea port waters as disclosed in Patent No. 2,200,469 of May 14, 1940.

For similar reasons an "electrodescaled" surface will be defined herein as a heavily rusted or corroded surface which has been treated by one or more of the processes disclosed in applications No. 526,621, No. 9,933, or Patent No. 2,200,469 until all or most of the firmly attached products of corrosion have been removed.

Also a "primer-type" of electrocoating will be defined herein as a non-metallic tough protective coating of two or more components which is capable of firmly bonding itself to the surface under treatment and to which additional more corrosion resistant electrocoating will firmly adhere when electrolytically deposited.

A study of the results obtained when electrodescaling heavily corroded steel surfaces such as the inside of high octane gasoline-carrying tank ship compartments indicates: (a) that sea water is one of the most effective electrolytes which can be used for this type of operation, (b) that, except for its prohibitive cost and the difficulties of storing and handling at different ports, a 3% solution of sodium chloride is almost as effective for electrodescaling, (c) that the presence of the chloride ion content of sea water is a greater aid to electrodescaling than an equal sulphate ion content, and (d) that acidified sea water is a considerably more effective descaling electrolyte and produces a more uniform descaling action than acidified hydrant water.

A study of the conditions for bonding sea water

electrocoatings to electrodescaled steel surfaces indicates that poor bonding is due to the deposition of an electrocoating on such a surface which is covered with a fine powder of loosely adherent particles of black oxide or carbon.

It appears that a marked improvement in bonding to such a surface can be obtained by the use of one or more of the procedures illustrated in the following examples and discussion:

Example 1.—A series of polished steel panels was subjected to a cathodic treatment at 400 milliamperes per square foot in natural sea water at $21 \pm 2^\circ$ C. in which the hydrogen ion content was varied from a pH of 9.5 to 2.7. For a specific set of conditions, when all factors were held constant except that the pH of the sea water was varied, the electrocoatings formed at the upper pH ranges of 9.5 were highly colloidal blue-white semi-translucent coatings. The electrocoatings became gray and completely opaque as the pH of the sea water was reduced from about 4.1 to 3.1. At these low pH values it appears that the non-metallic magnesium constituent is precipitated largely in microscopic crystals instead of in the colloidal form as at higher pH values. Below 3.0 very little deposit was obtained and below 2.7 no deposit of the typical magnesium-calcium electrocoating was formed.

An examination of these electrocoatings showed: (a) that the most adherent and best bonded coatings were formed at pH values between approximately 2.8 and 4.1; (b) that the coatings formed between pH values of approximately 4.1, or slightly greater to 5.5, had a minimum porosity and a maximum corrosion resistance; and (c) that above neutrality up to a pH of about 9.5 the electrocoatings became more colloidal.

Example 2.—A rusted steel panel was subjected to a cathodic treatment at 140 milliamperes per square foot in synthetic sea water held at temperatures of $21 \pm 2^\circ$ C. which contained 0.05% of hydrochloric acid. The pH value was 2.1 at the beginning of the test. After a twenty four hour period the pH value had increased to 2.6, and the brown rust layer had been removed, leaving a very thin black oxide layer. With further electrolysis a continuation of descaling occurred until the pH of the electrolyte increased to a value of about 2.8. At 2.8 and above a dark blue-green dense coating began to be deposited uniformly over the entire surface of the panel. This coating deposition continued until a pH of approximately 4.0, when the coating began to get lighter in color, indicating the deposition of the typical magnesium-calcium electrocoating. The treatment was continued until after 116 hours on test the pH had reached a value of 5.3 and the panel was uniformly covered with a gray, slightly green coating that was firmly bonded to the metal and very dense in structure.

After 21 months exposure in a corrosive industrial atmosphere of comparatively high humidity the coated surfaces were still well protected with a firmly bonded, dense hard orange gray coating. This type of treatment appears to have given excellent bonding and yet to have retained the valuable corrosion inhibiting properties of the typical magnesium-calcium electrocoatings.

Example 3.—A rusted steel panel was subjected to cathodic treatment at 140 milliamperes per square foot in synthetic sea water held at $21 \pm 2^\circ$ C. which had been acidified to give a solution containing 0.1% hydrochloric acid. The pH value was 1.9 at the beginning of the test. After a 24

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hour period the pH value had increased to 2.5 and essentially all of the black oxide layer was removed to bright clean metal. Electrolytic iron was deposited and descaling continued up to a pH value of about 2.8. At a pH value greater than 2.8 a dark blue-green dense coating began to form over the electrolytic iron and remaining thin layer of black oxide. It appeared that this action continued up to a pH value of 3.9 or slightly more. The treatment was continued until the pH reached a value of 5.3 as in the previous test. At the end of this 144 hour test the panel was uniformly covered with a firmly bonded dense multiple component type of coating similar to the previous test. After 20 months atmospheric exposure under the same conditions as Example 2 above, good corrosion inhibiting results were obtained and the coating was still firmly bonded.

Example 4.—Another rusted steel panel having the same amount and kind of corrosion was similarly treated in full strength synthetic sea water but without any acid addition. At the beginning of the test the pH was 8.6 and rose to slightly more than 9.5 at the end of the test. After a 24 hour period little descaling had taken place. After a 48 hour period slight spalling had taken place and after a 96 hour treatment considerable spalling had taken place and the surface was covered with a thin blue-gray coating. The treatment was continued for another 96 hours when the resulting magnesium-calcium electrocoating appeared to have about the same thickness as the coatings of Examples 2 and 3 above. However, after 18 months atmospheric exposure under the same conditions as Example 2, approximately 95% of the coating had spalled in flakes from $\frac{1}{8}$ to $\frac{1}{2}$ inch in diameter and the exposed surface had again rusted. A series of exactly similar tests in which the total ampere-hours of treatment was varied above and below that of Example 4 showed similar spalling and rusting of the spalled areas after 18 months atmospheric exposure.

A comparison of the observations enumerated in Examples 2, 3 and 4 above indicates the utility of these procedures, particularly when applied to the electrodescaling and electrocoating of such structures as tank ship compartments, tank car compartments and the like.

Although various test series have been made with synthetic and natural sea water acidified to different pH ranges from the normal value of about 8.0 down to 0.6, the following additional examples will further illustrate the procedures herein disclosed and claimed as new and useful.

Example 5.—A rusted steel panel was subjected to cathodic treatment at 140 milliamperes per square foot in synthetic sea water held at temperatures of $21 \pm 2^\circ$ C. which had been acidified with 0.52% hydrochloric acid. The resulting pH was 0.9 at the beginning of the test. After a 6 hour descaling time the pH had not changed and the panel was completely descaled to a clean bright surface. Although the acid partially dissolved the entire rust layer, the preferential solution of the ferrous oxide layer was indicated by tests for soluble iron. This panel became uniformly coated with a bright deposit of electrolytic iron which was well bonded to the panel like "flowed-on solder" under 60 magnifications. After 144 hours of cathodic treatment the pH had only increased to 1.6 hence this test was discontinued before the pH had reached the critical point of about 2.8 where the desirable non-metallic primer-type coating begins to form. After 20 months atmospheric exposure under the same

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conditions as Example 2 above the surface of this panel was heavily corroded.

Several series of tests were made in which synthetic sea water was acidified with sulphuric acid in exactly equivalent amounts as in the tests with hydrochloric acid. In each test substantially the same results were obtained as the corresponding test using hydrochloric acid.

Several series of tests were made on both rusted and polished panels at different current densities and temperatures in synthetic sea water to which small increments of iron salts were added until the equivalent iron concentration in the electrolyte was greater than 0.4%. Additions of both ferrous and ferric salts were tested. The following examples are illustrative of the desirable results obtained.

Example 6.—When cathodically treating polished panels at 140 milliamperes per square foot at $21 \pm 2^\circ$ C. in synthetic sea water to which ferrous chloride was added to give an equivalent iron content of 0.01% a thin light gray magnesium-calcium electrocoating was deposited. This coating was almost exactly the same as the typical gray-white magnesium-calcium electrocoatings produced by the methods of U. S. Patent No. 2,200,469 and had similar spalling characteristics.

Example 7.—When treating polished panels under exactly similar conditions except that the equivalent iron content was increased to 0.02% the resulting electrocoating was still quite similar to the typical magnesium-calcium electrocoating except that a considerable amount of a green iron compound was also electrolytically deposited. After exposure to the atmosphere this coating became a light orange. It appears that an electrocoating made from a sea water electrolyte begins to contain a useful amount of iron in the non-metallic form when the electrolyte contains 0.02% of iron in solution.

Example 8.—When cathodically treating both polished and rusted panels at 140 milliamperes per square foot at $21 \pm 2^\circ$ C. in synthetic sea water to which ferrous chloride was added to give an equivalent iron content of 0.04% a firmly adherent well bonded dark green coating was deposited on the panel. At this time the electrolyte contained both ferrous and ferric ions. With continued electrolysis the deposit became lighter in color and the soluble iron content of the electrolyte became negligible. After atmospheric exposure the surface of this multiple component coating changed color to a light golden orange. A considerable amount of the typical magnesium-calcium electrocoating was present in addition to the non-metallic iron content. In comparison to a typical gray two component magnesium-calcium electrocoating made under the same conditions but without soluble iron this coating was very tough and considerably better bonded to an electrodescaled surface. When the coating was scratched with a sharp point it came off in tough microscopic flakes rather than crumbling into microscopic particle aggregates. After a 20 month exposure to a moist industrial atmosphere this coating gave better corrosion protection to both the polished and the rusted electrodescaled panels than the corresponding coatings made from a pure solution of synthetic sea water.

When ferrous or ferric salt additions were made to an electrolyte, or a similar solution containing magnesium and calcium ions, the electrolyte was acidified at the beginning of a test to such a pH value that the respective iron ion was held in

solution and was not chemically precipitated. Similarly, when both ferrous and ferric salts were added the pH at the beginning of a test was reduced to a value below the precipitation point of the ferric ions. Such a form of an iron salt addition will give a specified equivalent iron ion content with a minimum waste.

For a specific total amount of ferrous and ferric salt additions to the electrolyte under test an increase in the ferric ion content caused a desirable increase in the colloidal iron content of the resulting non-metallic magnesium-calcium-iron electrocoating. Such a treatment further improved the toughness of the resulting primer-type of magnesium-calcium-iron electrocoating and its adhesion to the metal surface under treatment.

Similar tests using variations of soluble iron content in sea water showed that when the equivalent iron content was increased to values greater than about 0.4% the cathodic reaction rapidly changed from a deposition of the non-metallic magnesium-calcium-iron primer-type of coating to a deposition of electrolytic iron. Under these conditions a useful corrosion inhibiting coating was not formed, hence a soluble iron addition greater than 0.4% was found to be undesirable.

Additional tests in sea water when this soluble iron content was held constant, and the current density and temperature was varied, confirmed the preferred ranges of current density as disclosed in U. S. 2,200,469 and applications, Serial No. 526,621 and Serial No. 9,933.

The value and utility of electrocoatings deposited from sea water with equivalent amounts of either of the iron sulphate additions appear to be similar to the corresponding chloride salt additions. Hence for the treatment of tank ships and other tank compartments either the chloride or sulphate may be used depending on which is the cheaper salt. Similarly, the cheaper acid may be used as found desirable.

Although not essential, it has been found generally desirable to add a mineral acid rather than the iron salts of the acid. The acid addition produces a cleaner surface for the electrocoating deposition by its attack chiefly of the ferrous oxide layer of the rust deposit. By so doing the iron salts which are required for the non-metallic electrocoatings are produced. It should be noted that the complete conversion of 0.52% of hydrochloric acid to ferrous chloride will give an electrolyte containing 0.4% of ferrous ions. Quantities in excess of either of these values have been found to give undesirable electrocoatings and should be avoided.

If desired, cathodic treatment can be omitted during the period while the acid attacks any corrosion products and until the pH of the electrolyte reaches 2.8. However, if the surface is cathodically treated during this period a thin deposit of electrolytic iron will form which has beneficial results. In other words, the electrolyte can be acidified to a pH value greater than 1.1 and less than 2.8. The solution can then be allowed to react with any corrosion products on the metal surface until the pH value has increased to 2.8. The surface can then be cathodically treated at a sufficient current density and at a pH value of 2.8 or more but less than 4.1 to deposit thereon a firmly bonded and adherent, although somewhat porous, coating consisting essentially of low soluble magnesium-calcium and iron compounds. The hydrogen ion concentration of the solution can then be further reduced to a pH value greater than 4.1 and less than 5.5 while it is cathodically

treated at a current density which will deposit a dense highly corrosion resistant basic non-metallic coating of calcium and magnesium on and in the pores of the previously deposited firmly bonded somewhat porous primer-type coating.

The cathodic treatment which is carried out at pH values between the limits of 4.1 or slightly higher and 5.5 should be made at a current density within the limits of 30 to 400 milliamperes per square foot when using sea or sea port water at its ambient temperature as for example when pumping such an electrolyte into a tank ship compartment. More specifically the conditions should be those defined in U. S. Patent 2,200,469.

If this latter operation is carried out with electrolytes containing calcium and magnesium ions held at temperatures above ambient temperatures then the cathodic current density should be set at a value within the limits of the relationship between these two variables as defined and delineated in patent applications No. 526,621 or No. 9,933. This relationship may be expressed by the equation $T = 34 \log_{10} X + C$ wherein T is the temperature of the electrolyte in degrees centigrade, X is the cathode current density in amperes per square foot, and C is a constant within the range of 30 to 70.

Where a synthetic electrocoating solution containing magnesium and calcium ions with or without iron ions is used it is intended that the concentrations of the magnesium and calcium ions be as defined in applications No. 526,621 or No. 9,933. In other words, such an electrolyte is to contain magnesium and calcium ions in sufficient quantity for plating action to occur; or in concentrations at least equal to those values found in sea and seaport waters; or even more concentrated solutions of these ions.

Other tests with sea water electrolytes at $21 \pm 2^\circ \text{C}$. which have been acidified with hydrochloric or sulphuric acid show that between the pH ranges of 1.1 and 2.3 a mild steel surface will be attacked at a nominal rate of about 128 milligrams per square decimeter per day or less and yet any black oxide remaining on an electrolytically descaled surface will be dissolved and any carbon particles detached. However, as the acid content is increased to give pH values less than 1.0 the rate of attack of the steel surface increases rapidly and becomes excessive at many times the above rate. The upper chemical descaling limit is reached when the pH of these solutions containing magnesium and calcium ions climbs to a value of 2.8; the descaling action stops and cathodic non-metallic well bonded primer-type coatings can then be formed.

With regard to the comparative inhibiting value of sea water and fresh water similar tests show that for the same pH value within the range of 1.1 to 2.3 the rate of attack of a steel surface will be more than twice as great when fresh potable water is used.

A preferred procedure may be summarized as follows: When an inside tank surface such as a tank ship compartment which is to be electrocoated is badly corroded and covered with a very heavy firmly attached layer of rust, as is often encountered, it is not essential but usually desirable to descale the surface in accordance with a cathodic treatment as set forth in U. S. No. 2,200,469. The resulting descaled surface will be free of the products of corrosion except for a thin black powdery or granular deposit containing iron, carbon or both. After removing the resulting piles of rust flakes and scale and arrang-

ing the proper anode system, the tank is filled with sea water or an equivalent electrolyte which has been acidified to give a hydrogen ion concentration which has a pH value of more than 1.1 and less than 2.8. Up to a pH of 2.8 chemical descaling takes place. The surfaces are then subjected to a cathodic treatment at a sufficient current density and at a pH value of 2.8 or more but below approximately 4.1 to deposit thereon an adherent firmly bonded primer-type electrocoating. The pH value of the electrolyte is then slowly increased to a value greater than 4.1 and less than 5.5 and the surface is subjected to a current density which will deposit on and in the pores of the primer-type coating a firm dense adherent protective coating consisting essentially of basic magnesium and calcium compounds. If the time required to reach a value of 5.3 or 5.5 is excessive as illustrated in Example 5 above, a neutralizing agent may be slowly added. A carbonate, hydroxide or oxide of an alkali or alkaline-earth metal is suitable. However, a more desirable way of decreasing the time required for this operation is to add less acid at the beginning and thereby begin the operation at a pH value which will essentially dissolve the oxide scale, such for illustration as given in Example 3. Although the initial pH values are not critical, those less than 0.9 have not given satisfactory results without the use of a neutralizing agent, hence are uneconomical.

In the above preferred procedure the following separate operating steps are noted: (a) Preferably with a heavy rust scale of say $\frac{1}{8}$ inch thick or more the surface is electrolytically descaled, and the loose scale removed; (b) the surface is treated with a sea water electrolyte, or its electrochemical equivalent, which has been acidified with mineral acids to give a pH value greater than 1.1 and less than 2.8; (c) although not a required step during a part or all of this period, the surface may be subjected to a cathodic current density which will deposit electrolytic iron on the surface under treatment, thereby decreasing the amount of metal loss and aiding the mechanical prying action of the liberated hydrogen gas in removing any remaining difficultly soluble corrosion products; (d) at and above a pH value of 2.8 and below values averaging about 4.1 the surface is subjected to a cathodic treatment which will deposit a primer-type of non-metallic electrocoating containing iron, magnesium and calcium having fair corrosion inhibiting properties but which is tough, highly adhesive and firmly bonded to the surface under treatment; (e) the same treatment is then continued at the preferred current densities defined in U. S. No. 2,200,469 or application No. 526,621 or No. 9,933 at pH values greater than 4.1 and less than 5.5, thereby effecting a change from the primer-type of electrocoating to the denser type of magnesium-calcium electrocoating having low porosity and good corrosion inhibiting properties; and (f) for a given ampere-hour expenditure it appears that a minimum of porosity is obtained if the treatment is stopped at any pH value above 4.1 and below 5.5; however, the deposition can be continued at higher values without apparent damage.

If iron salts are added to sea water or to a magnesium-calcium containing electrolyte as disclosed herein the first steps, (a) and (b), of the preferred procedure described above may be omitted. In this case the primer-type of electrocoating can be deposited directly from such

a solution, and with a depletion of the iron content the deposit will change into the desired low porosity non-metallic magnesium-calcium electrocoating, provided the current density is within the ranges claimed in U. S. No. 2,200,469 or application No. 526,621 or No. 9,933. If the equivalent iron content of these ferrous salt additions is greater than about 0.4% no useful non-metallic primer-type of electrocoating will form, but electrolytic iron will be deposited. However, if the iron content of such additions is in the order of 0.4% to 0.2% well bonded non-metallic primer-type coatings can be cathodically deposited. As the additions are varied from ferrous to ferric ions the toughness of the deposit is considerably increased and it becomes less friable. However, the primer-type coating with the best bonding and greatest toughness appears to be formed when the iron addition is a mixture of both ferric and ferrous ions.

It is thus seen that a corroded mild steel surface can be treated by the processes herein disclosed, with the following results: (a) a non-metallic three component primer-type of electrocoating having fair corrosion inhibiting properties and excellent bonding, adhesive and toughness characteristics is deposited, and (b) a typical highly protective, non-metallic magnesium-calcium electrocoating of low porosity is then deposited. Therefore this improved composite electrocoating has characteristics not found in any previously known non-metallic magnesium-calcium electrocoating. The novel essential of this useful composite electrocoating resides in the methods of formation and composition of the intermediate layer of the primer-type of multiple component electrocoating as herein defined.

If desired the firmly bonded primer-type of electrocoating containing the low soluble iron compounds may be electroplated on an iron or steel surface to be protected at one time and then at a later period this coating may be treated with the regular electrocoating procedure defined in the patent or applications referred to herein. For this type of operation the iron ions may be added by interaction of the hydrogen ions with any corrosion products, with the surface to be electrocoated, or by an addition of the desired iron salts.

The required cathodic current for depositing these electrocoatings may be supplied by the use of either: (a) suitably positioned driven anodes powered from an external source, or (b) suitably positioned sacrificial galvanic anodes, provided the galvanic electromotive force generated is sufficient to supply the required cathodic current density.

When desirable other mineral acids such as nitric and phosphoric may be used instead of hydrochloric or sulphuric acid; also the iron salts of these acids may be used. In general the use of hydrochloric, or sulphuric acid, or their iron salts will be found to be the most economical for the preparation of these coatings on large surfaces. However it is intended that the term "mineral acids" include the use of one or more of these acids. Similarly it is intended that one or more of the iron salts of these acids may be used singly or in combination, or in combination with one or more of these acids.

While certain desirable embodiments of the invention have been illustrated and described by way of example, it is to be understood that the invention is broadly inclusive of any and all modi-

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fications falling within the scope of the appended claims.

I claim:

1. The process of forming a firmly bonded electrocoating on the surface of a ferrous metal structure which is in contact with an enclosed body of an electrolyte essentially composed of sea water and which comprises the steps of adding a sufficient quantity of at least one of the mineral acids to give a hydrogen ion concentration between 2.8 and 4.1 on the pH scale and of adding a sufficient quantity of at least one of the iron salts of a mineral acid to give an equivalent soluble iron content greater than 0.02% and less than 0.4%, then making the surface cathodic at a sufficient current density to deposit thereon a firmly adherent coating which consists substantially of a mixture of water-insoluble compounds of iron, magnesium, and calcium.

2. The method of descaling and then electrocoating the surface of a corroded and rust-covered ferrous metal structure which is in contact with an enclosed body of an electrolyte essentially composed of sea water which comprises the steps of acidifying the electrolyte to a pH value greater than 1.1 and less than 2.8 with a mineral acid, whereby the acid content of the electrolyte

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reacts with the rust on the ferrous metal surface until the pH reaches a value of approximately 2.8 and the soluble iron content attains a value greater than 0.02% and less than 0.4%, then making the surface cathodic at a sufficient current density to deposit thereon a firmly adherent porous coating which consists substantially of a mixture of water-insoluble compounds of iron, magnesium, and calcium, adding a neutralizing agent to bring the hydrogen ion concentration of the electrolyte to a pH value between 4.1 and 5.5, and then densifying the coating by cathodically forming in its pores a composition comprising a mixture of water-insoluble compound of magnesium and calcium.

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2,444,174	Tarr et al.	June 29, 1948
2,534,234	Cox	Dec. 19, 1950

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