Dec. 6, 1955 W. H. PRINE 2,726,201

ANODIC PICKLING AND NICKEL PLATING OF TANK INTERIOR USING SINGLE ELECTROLYTE

Filed Aug. 2, 1950 2 Sheets-Sheet 1

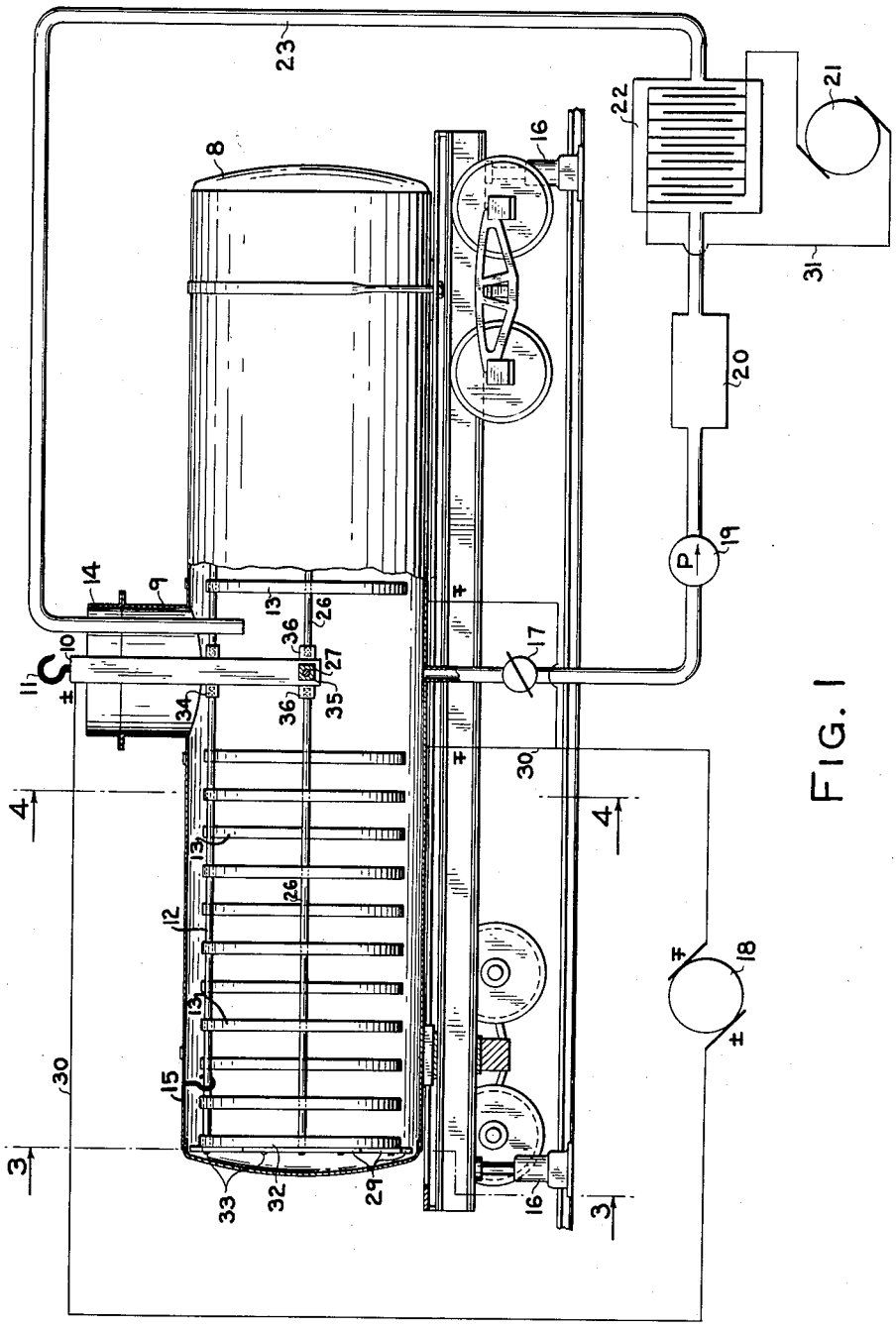



FIG. 1

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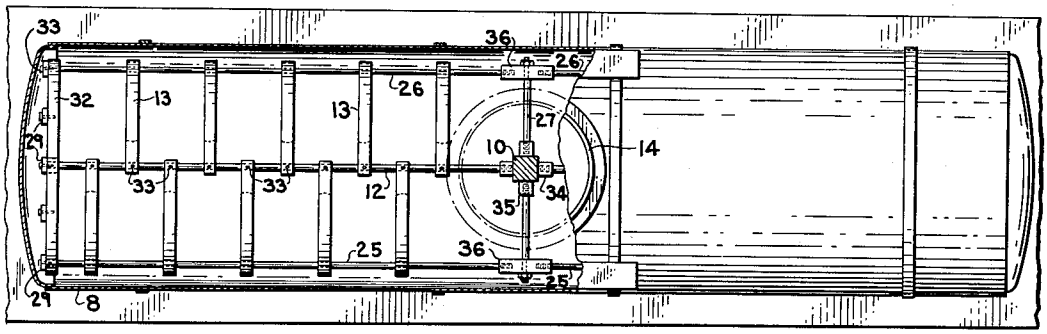



FIG. 2

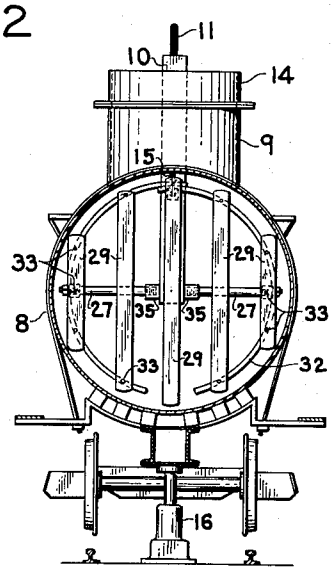



FIG. 3

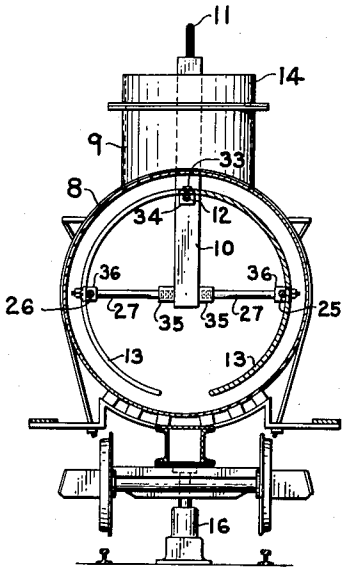



FIG. 4

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2,726,201

# ANODIC PICKLING AND NICKEL PLATING OF TANK INTERIOR USING SINGLE ELECTROLYTE

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1 Claim. (Cl. 204—26)

The present invention relates to a process for producing metallic linings on the interiors of large metallic containers such as are used in chemical process industries and in railway and truck tank cars and, more particularly, to a process for producing electroplated metallic linings in large metallic containers for transporting and storing corrosive chemicals.

It is well known that large metallic containers are employed as railway and truck tank cars for transporting various corrosive chemicals, such as acid and alkali solutions, petroleum products, and corrosive food products. In transporting corrosive products, it is necessary to employ containers of special construction which will be resistant to the corrosive action thereof. In this connection, the transportation of high purity alkali and acid solutions in tank car containers has always presented a problem in that it has been difficult to avoid tank car container corrosion. Of even more importance than the actual corrosion problem, it has been very difficult to avoid the contamination of alkalis, acids and other high purity products which are transported with deleterious elements such as iron, copper, zinc, etc., which enter the alkalis and acids from the containers because of the corrosive action of the products. Caustic soda of high purity is employed in the manufacture of textiles, soaps, paper, etc., and it is necessary to use caustic soda of high purity, especially caustic soda substantially devoid of iron and other deleterious elements, in order to produce good quality products in the aforementioned fields of manufacture. For example, in the production of rayon a desirable "Rayon-grade" caustic of from about 70 to about 73 per cent concentration contains iron from about 2 to about 5 parts per million. It is obvious that these commercial requirements in the rayon industry demand caustic substantially devoid of iron, and it is essential that during shipment these caustic solutions not pick up substantial iron content.

It was formerly the practice to ship caustic soda solutions of low concentration in tank cars. However, this method of shipment was not very economical in view of the low concentration of caustic soda and high volume of liquid for a given weight of caustic involved. As new and improved methods were developed in the manufacture of high purity caustic soda soluations of high concentration, e. g., 50% to 73% concentration, the problem of transportation economics was ameliorated. The transportation of caustic soda solutions of 50% to 73% concentration, while it solved the freight cost problem, only served to intensify the corrosion problem of the caustic containers used to transport and to store these caustic soda solutions and, in addition, also served to intensify the problem of contamination of the caustic solution with iron and other elements. Presently, solutions of upwards to 80% concentration of caustic soda have been transported for some commercial uses; but this concentration of caustic soda had to be handled at temperatures up to 200° F., and in some instances as high as 275° F., for at ordinary room temperatures concentrated caustic soda of from about 73% to about 80% concentration is solid. These solutions, when handled hot to facilitate the loading and unloading of tank cars, were sufficiently corrosive to metallic containers to cause undesirable contamination of the caustic by corrosion products, especially iron. Under



these conditions, the contamination pickup in these hot solutions was considerable.

Attempts were made to solve this problem by using tank cars of special construction. However, these specially-constructed containers required the use of special fabrication procedures which added to the final cost of the tank cars. Alternative methods were proposed to solve the problem by employing special processing techniques and methods for converting ordinary steel tank cars in situ into corrosion resistant containers for transporting hot caustic soda solutions of high concentrations. One proposed method comprised applying adherent non-metallic coatings, e. g., such coatings as rubber latex or polystyrene compositions, to the interior surface of the metallic tank cars. However, these coatings usually did not function properly, usually did not have good service life, and, because of the relative weakness of the linings, were subject to accidental breaking and cracking in tank car service which is unusually severe as compared to the service required of stationary containers. These non-metallic linings were also subject to failure caused by the subsequent undercutting of the coatings by corrosive action of caustic soda solutions. Furthermore, in the chemical process industries, food industries, etc., a demand for plating in situ large containers with nickel has existed; and with increasing process developments, the demand for plating large vessels in position with nickel has increased. For example, large storage vessels which were fabricated in position for use in storage of one non-corrosive chemical cannot be employed for storage of newly developed corrosive chemicals for the chemicals will be contaminated with constituents from the vessel walls. Nickel is a desirable passive lining for most metallic containers, but it has been difficult to plate these large vessels in position with nickel. The demand is therefore great for a process and apparatus for plating in position these large chemical process containers.

Endeavors have also been made in the application of nickel linings to tank cars in situ and to other large vessels in position to overcome the foregoing disadvantages inherent in the use of linings enumerated heretofore. No satisfactory method has been developed for applying in one manipulation the complete nickel lining to the interior of large containers in position and especially to tank cars in situ so as to give satisfactory results. Thus, conventional electroplating methods could not be employed successfully to produce good adherent corrosion-resistant metallic linings on the interior of these large containers in position. For example, when coating small articles with nickel by electrodeposition from a nickel electrolyte, the usual procedure comprised cleaning the articles in an alkaline type of cleaning solution, i. e., caustic solution, to free them of organic contaminating substances, rinsing with water to remove the alkali, and then removing all oxide and objectionable metallic oxide films in a separate aqueous solution by anodic pickling or by other suitable pickling means, removing said article from the solution and washing it free from adhering pickling solution and pickling sludge, transferring said article to a nickel electrolyte, and plating thereon a deposit of nickel. However, the foregoing plating procedure was not successful when employed to produce satisfactory nickel deposits on large metallic containers such as are employed in tank cars. The transfer time required for rinsing with water and replacing large volumes of pickling solution with large volumes of plating solution in large containers and especially tank cars was considerable, and this permitted re-oxidation of the pickled steel. As a result, the adhesion of the nickel electroplate obtained by this plating method requiring removal of pickling solutions, water rinsing, and replacement with plating solution was poor. Furthermore, the electroplate

flaked badly and did not prevent corrosion of the underlying surface. In view of the foregoing, the art has realized that there is a need for successfully obtaining a nickel lining within large containers in position, and especially tank cars. The art has realized that a lining is needed which will not only be resistant to corrosion by chemicals, such as hot concentrated caustic soda solutions, food products, etc., but which would also be strongly adherent and therefore be capable of withstanding the rough treatment to which tank cars are subjected. In addition, a lining is needed which will be capable of giving good service life.

I have discovered a process whereby a strongly adherent, corrosion-resistant lining of nickel can be applied to the interior surface of large steel containers, such as tank cars, by electroplating in situ, which lining when applied overcomes the objectionable features of the prior art discussed hereinbefore.

It is an object of the present invention to provide a large container lining which is resistant to corrosive chemicals, such as concentrated solutions of caustic soda, and petroleum products.

Another object of the invention is to provide a corrosion-resistant metallic tank car lining which is strongly adherent and which possesses good service life.

The invention also contemplates providing an electrolyitc process for applying a corrosion-resistant metallic nickel lining to large containers, such as are employed in tank cars, having good rupture strength and being capable of withstanding the usual rough treatment to which tank cars are subjected.

It is a further object of the invention to provide an electrolytic process for applying a corrosion-resistant lining in situ to large containers such as used in tank cars, chemical process industries, and the like.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawings, in which:

Figure 1 represents a diagrammatic illustration of an installation such as is employed in carrying out the present invention;

Fig. 2 is a plan view of the particular anode structure showing in detail the anode structure employed in carrying out the practice of the present invention;

Fig. 3 is a sectional view taken on line 3—3 of Fig. 1; and

Fig. 4 is a sectional view taken on line 4—4 of Fig. 1.

Generally speaking, the present invention contemplates a process for the application of a corrosion-resistant metallic nickel lining to metallic container interiors in situ, i. e., iron, steel, etc., containers. The coating consists of a continuous adherent nickel lining which is applied electrolytically by employing a nickel-containing electrolyte which is contained within the metallic container. Broadly stated, the process comprises mechanically cleaning the interior surface of a large container, such as used in tank cars, by suitable means, such as sand blasting, shot blasting, etc.; suspending in said container a demountable skeletonized electrode structure adapted to distribute current substantially uniformly over the interior surface to be plated; filling the interior of the container with an acid nickel-plating electrolyte; anodically pickling the interior of the container by employing the nickel-plating electrolyte as the pickling solution and by passing an electric current from the tank car container through the electrolyte within the tank car container to the suspended electrode structure, i. e., make the tank anodic with respect to the electrode structure; and without removing the electrolyte from the container, reversing the current to pass a plating current from said suspended electrode structure through said nickel electrolyte to the clean interior surface of the container to electroplate nickel from said electrolyte onto the interior surface of the tank car container while agitating said electrolyte by suitable means. The foregoing process insures the production of a strongly adherent uniform nickel lining in situ. By carrying out the invention in the aforementioned manner, re-oxidation and passivation of the cleaned steel of the interior surface of the metallic container subsequent to the pickling operation are prevented and a very adherent electroplate of nickel is obtained having good corrosion resistance and being capable of giving good service life.

Referring to the drawings, a diagrammatic illustration of an installation such as may be employed in carrying out the practice of the present invention is shown wherein reference character **8** represents a tank car container. Assembled within the tank car container **8** is a demountable skeletonized anode structure having an external configuration substantially that of the internal configuration of tank car container **8**. The anode structure consists of a supporting central spine anode support **10** having an insulated hook **11** attached thereto and internally threaded collars **34** and **35** welded thereon. The central spine support **10** is rigidly connected to an upper internal longitudinal anode support **12** and a mid-section lateral anode support connecting member **27**. Longitudinal anode support **12** is rigidly connected to the central spine support by being sectioned into two pieces and being threaded into the internally threaded collar **34**. Also, the connecting member **27** is sectioned into two pieces and is rigidly connected to central spine support **10** by being threaded into internally threaded collar **35**. Each end of the mid-section lateral support connecting member **27** is rigidly connected to substantially the mid-sections of side longitudinal anode supports **25** and **26**. Side longitudinal anode supports **25** and **26** are each sectioned in two sections to provide ease of insertion and removal. The sections are joined together by being threaded into internally threaded collar **36** to provide complete rigid members **25** and **26** within tank car container **8**. The ends of the longitudinal anode supports **25** and **26** are rigidly connected at substantially the mid-sections of end arcuate anodes **32** which being assembled substantially define the end circumferential contours of the tank car container **8**. Preferably, anode supports **10, 12, 25** and **26** are insulated. Vertically rigidly connected along the plane surface of end arcuate anodes **32** are anodes **29**, said anodes **29** being spaced and arranged so as substantially to define the end portion areas of tank car container **8**. Alternately spaced and rigidly connected to the longitudinal anode supports **12, 25**, and **26** are arcuate anodes **13** substantially defining the entire longitudinal internal contour of the tank car container **8**. The individual members of the entire anode structure are rigidly attached one to the other by connecting pins **33** or by any other connecting means, such as bolts, screws, etc. The assembled anode structure as described hereinafter is partially supported and centrally located within the tank car container **8** by insulated hooks **15** connected in position onto the upper inner surface of the tank car container **8** substantially near the ends of the longitudinal anode support **12**. The large spine hook **11** rigidly connected to the central spine **10** supports most of the anode structure weight. The large supporting hook **11** is positioned by any supporting means. An electrical circuit **30** is connected to the central spine support **10**, the tank car container **8**, and an electrical generator **18**. An electrolyte transfer fluid circuit is provided through tank car container **8**, conduit piping **23**, including a shut-off valve **17**, a force pump **19**, a filter **20**, and an auxiliary electrolytic cell **22** to remove iron from the electrolyte, connected in series and in the order named. The electrolytic cell **22** has an electrical circuit **31** connected to an auxiliary electrical generator **21**. The tank car container **8** is provided with supporting hydraulic jacks **16** at each end of the tank car container. A manhole opening **9** is provided with a removable extension **14** having a circumferential contour equal to the circumferential contour of manhole opening **9**.

In performing a nickel-plating operation upon the internal surface of tank car container **8**, the container is first mechanically cleaned as by shot blasting, sand blasting, etc. The anode structure described hereinbefore is then assembled, suspended, and supported within tank car container **8** by hooks **11** and **15** and the container filled to the top of extension **14** with a nickel-plating electrolyte. Current from generator **18** is passed from the tank car container **8** through the electrolyte, through the anode structure as described hereinbefore, and through the electrical circuit **30** back to electrical generator **18**. This electrical current is provided for a time required to pickle the interior surface of tank car container **8**. This electrolytic pickling operation using the plating electrolyte cleans the surface as described hereinafter. While this pickling operation is performed, it is preferred to "rock" the tank car container **8** by alternately actuating the hydraulic jacks **16**. During the pickling and plating operations, valve **17** is opened and pump **19** is operated to circulate the electrolyte through the filter **20** and the electrolytic cell **22**. This continuous circulation of the electrolyte through the pump **19**, filter **20**, and cell **22** continuously provides agitation of the electrolyte. The action of the force pump **19** transfers the electrolyte in tank car container **8** through filter **20** wherein sludge, sediment, and any other mechanical particles are removed. The electrolyte then passes through electrolytic cell **22** and auxiliary electrical generator **21** is operated to produce an electrolytic current through cell **22**. Iron and other metallic impurities, which have been picked up in the pickling operation in tank car container **8**, are plated out at the cathodes in cell **22**, and the electrolyte passes through conduit **23** back into container **8** through manhole opening **9**. After the pickling operation is performed, the plating operation is begun. The current is reversed from the electrical current direction employed in the pickling operation so that the current now flows to and through the anode structure to the tank car container **8**, through the electrical circuit **30** back to electrical generator **18**. By employing this current flow, nickel is plated from the electrolyte in tank car container **8** onto the clean pickled interior surface of the tank car container **8** to form a nickel-plated lining thereon. Tank car container **8** is "rocked" by hydraulic jacks **16** during the plating operation to remove any gas pockets and to agitate the electrolyte. Continuous circulation of the electrolyte through conduit **23** also provides agitation. After the plating operation has been performed, the electrolyte is pumped out of the tank car container **8** and the anode structure is disassembled and removed to be used in other plating operations.

It is an essential feature of the present invention that the anodic pickling operation and the nickel electroplating operation be accomplished consecutively in the same electrolytic bath without removing the bath from the tank car. In order to obtain an adherent nickel plating, it is necessary that the steel surfaces on which the nickel plating is to be electrodeposited be clean and free of oxide films, etc., which produce poor adhesion between the tank surface and the electrodeposit. The interior of the tank car is first mechanically cleaned, e. g., by sand blasting, shot blasting, etc., to remove the mechanically adherent oxides, such as mill scale, coarse rust, etc. Thereafter, the surface is treated by anodic pickling in the nickel-plating electrolyte which is employed in the process to remove the microscopic surface films which passivate the surface and interfere with the production of an adherent nickel plate. In order to prevent the formation of other passivating films, after the anodic pickling operation required by the invention, the electroylte is kept in constant protective contact with the cleaned container surface.

In carrying the invention into practice, an acid nickel-plating bath selected from the group consisting of the sulfate-chloride baths and chloride baths may be employed successfully. For example, good nickel adhesion is obtained when using an aqueous plating bath comprising about 150 to about 500 grams per liter of nickel sulfate, from about 20 to about 65 grams per liter of nickel chloride, and from about 15 to about 45 grams per liter of boric acid, the pH of said bath being maintained from about 1.0 to about 4.5. Another satisfactory plating bath contains about 300 grams per liter of nickel chloride and about 30 grams per liter of boric acid and has a pH of from about 1.0 to about 3.5. A preferred plating bath contains about 150 to about 300 grams per liter of nickel sulfate, from about 15 to about 30 grams per liter of nickel chloride, about 30 grams per liter of boric acid and has a pH maintained at about 2 (electrometric).

When one of the foregoing solutions is used for the dual purpose of anodically pickling and nickel plating the interior surface of a tank car, the pH range of the solution is maintained at about 1.0 to about 4.5 (electrometric). However, for best results, it is preferred that the pH range of the solution be maintained as low as is consistent with obtaining good nickel deposits, e. g., at a pH of about 2.0. The current density which is employed during the anodic pickling operation may range from about 5 amperes per square foot (a. s. f.) to about 50 a. s. f., and preferably at about 10 a. s. f. Too high a current density will result in an excessive dissolution of iron into the plating solution. The time interval in the operation during which the steel surface is de-passivated and electrolytically cleaned depends on the character of the steel surface, bath temperature, current density, etc. In general, when employing the foregoing current densities, the anodic pickling time may range from about 15 seconds to about 120 seconds, and preferably about 30 seconds. It is desirable that the anodic pickling time should not be below about 30 seconds at a current density of 10 amperes per square foot in order to secure desirable pickling of the container interior. The upper limit of pickling time is dependent upon various factors, e. g., type of material, solution concentration, the need for minimizing iron pickup in the electrolyte, etc. When the interior surface of the tank car has been sufficiently pickled, the current is reversed, the tank car is made cathodic, and nickel is electroplated thereon. When long pickling times are used during the anodic pickling operation, it is preferred not to reverse the current immediately but rather to stop the pickling operation for a sufficient length of time in order to allow the anodic film which forms next to the interior surface of the tank car to diffuse into the solution body. This holding period between the anodic and cathodic application of current to the tank surface can be shortened or dispensed with by continuously agitating the solution during the anodic pickling operation. Holding periods of up to about 60 seconds may be used as desired, although longer periods of time may be used without any detrimental effects. With good solution agitation, a holding period of at least 3 seconds is advantageously employed to provide diffusion of substantially all the anodic film into the solution body. This time may be shortened by increasing the degree of agitation. The electrolytic bath temperature for the anodic pickling operation should be maintained within the range of about 70° F. to about 160° F. The temperature of the electrolyte during the plating operation may be maintained from about 70° F. to about 160° F. with an optimum temperature within the range of from about 70° F. to about 90° F. when employing a current density of about 10 a. s. f. If it is desirable to perform the plating quickly, a faster plating rate may be provided by heating the electrolyte to a temperature from about 130° F. to about 140° F. and employing a current density within the range of from about 40 amperes per square foot to about 50 amperes per square foot.

Upon completion of the anodic pickling operation, the tank car is made cathodic by reversing the current and nickel is electroplated onto the interior surface of the tank car without removing the nickel solution from the tank car. The current density employed during the plat-

ing operation is controlled within the range from about 5 a. s. f. to about 100 a. s. f., and preferably at about 10 a. s. f. when the lower temperature range is employed. The plating operation is continued until a thickness of at least about 0.01 inch is obtained which may be increased to about 0.06 inch, depending upon the length of time the current is applied. In practicing the plating operation, a plating time of about 20 hours at a current density of 10 a. s. f. will generally provide a deposit of nickel of 0.01 inch and if a current density of about 50 a. s. f. is used, a plating time of about 4 hours will provide a 0.01 inch deposit of nickel.

In order to obtain a uniform nickel plate on the interior surface of a tank car, it is necessary to use an anode or anodes having, in general, an external contour configuration substantially that of the interior of the tank car so as to maintain a substantially uniform distance between the anode and the cathode surface area and also to effect a uniform distribution of current and uniform deposit thickness during the plating operation. Insoluble anodes, such as lead, or soluble nickel anodes may be used in carrying out the plating operation of the invention. If insoluble anodes are used, frequent additions of nickel ions should be made to the nickel bath by adding nickel carbonate or by solution of nickel in an auxiliary regenerative unit. In order to compensate for the nickel ions depleted in the bath during the plating operation, it is preferred to use soluble nickel anodes supported on wrought nickel supports which are insulated except where the anodes make contact with the anode supports. It is not contemplated that the anodes will be removed during the plating operation, and the solution within the tank car container should be rocked at intervals in order to displace any hydrogen gas which may tend to be trapped as "pockets" under the top surfaces of the container during the plating operation. Rocking can be accomplished with the use of any suitable rocking means, such as hydraulic jacks. The solution can also be agitated by circulation pumping by using any suitable pumping means to provide a circulation of the solution.

In the application of the process described hereinbefore to SAE 1030 steel using an electrolytic bath consisting of 300 grams per liter of nickel sulfate, 30 grams per liter of nickel chloride and 30 grams per liter of boric acid, said electrolyte having an acidic concentration at which the pH of the bath was about 2.0 and being at a temperature of about 70° F., a continuous nickel plate was obtained having an adhesion value of about 54,000 pounds per square inch. An electrolytic bath consisting of 150 grams per liter nickel sulfate, 15 grams per liter nickel chloride and 30 grams per liter boric acid, said electrolyte having a pH value of about 2.0 provided a nickel lining having an adhesion value of about 91,000 pounds per square inch. In carrying out the anodic treatment step of the process, the current density was maintained at about 10 amperes per square foot for about 30 seconds. A cathodic plating operation was carried out in each case with the current being maintained at about 10 a. s. f. until the nickel linings, having the adhesion values described hereinbefore, were secured.

The present invention is particularly applicable to tank car containers used in shipping corrosive chemicals, such as solutions of caustic soda, acids, petroleum products, chemicals and other food products. By using the process of the invention disclosed hereinbefore, it is possible to convert tank car containers heretofore not usable for transporting caustic soda and other highly corrosive substances into corrosion resistant containers by electroplating the interior surface of tank cars with a strongly adherent, corrosion-resistant lining of nickel. The nickel electroplate obtained by the process described hereinbefore is continuous throughout the interior of the tank car and is uniform in composition throughout. Furthermore, the present invention is particularly applicable to plating metallic containers in position without disassembly or refabrication of the metallic container in order to perform the plating operation.

It is to be noted that the present invention is not to be confused with prior methods of obtaining by electrolytic means strongly adherent nickel plate, in that in this inventive process the anodic cleaning step employed in the process is carried out in the same bath from which the nickel electroplate is obtained without removal of the electrolyte bath from the container during the pickling and plating steps.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claim.

I claim:

A process for electrolytically depositing a thick, corrosion-resistant layer of nickel on the interior surface of a large steel tank in situ which comprises, in combination, the steps of assembling and suspending an electrode structure in the cavity defined by the interior surface of said tank, filling said tank with an aqueous acid nickel-plating electrolyte having a pH of about 1 to about 4.5 and containing about 150 to about 500 grams per liter of nickel sulfate, about 20 to about 65 grams per liter of nickel chloride and about 15 to about 45 grams per liter of boric acid, passing an electric current for at least 15 seconds through said tank, electrolyte and electrode structure in a direction such that the interior surface of said tank contacted by said electrolyte becomes the anode and is anodically pickled over substantially all portions thereof simultaneously, subsequently passing an electric current through said tank, electrolyte and electrode structure in a reverse direction such that the interior surface of said tank contacted by said electrolyte becomes the cathode and nickel is electrolyticaly deposited over substantially all portions thereof simultaneously, maintaining the current in the latter direction until a corrosion-resistant layer of nickel of a thickness of at least about 0.01 inch is built up by electrolytic deposition on substantially all portions of the interior surface of said tank contacted by said electrolyte, and removing said electrolyte from said tank, whereby a thick, corrosion-resistant layer of nickel is electrodeposited on the interior surface of said tank while using the same acid nickel-plating electrolyte for the dual purpose of anodically pickling and of electroplating the interior surface of the tank without emptying the electrolyte from the tank between the pickling and plating operations.

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