

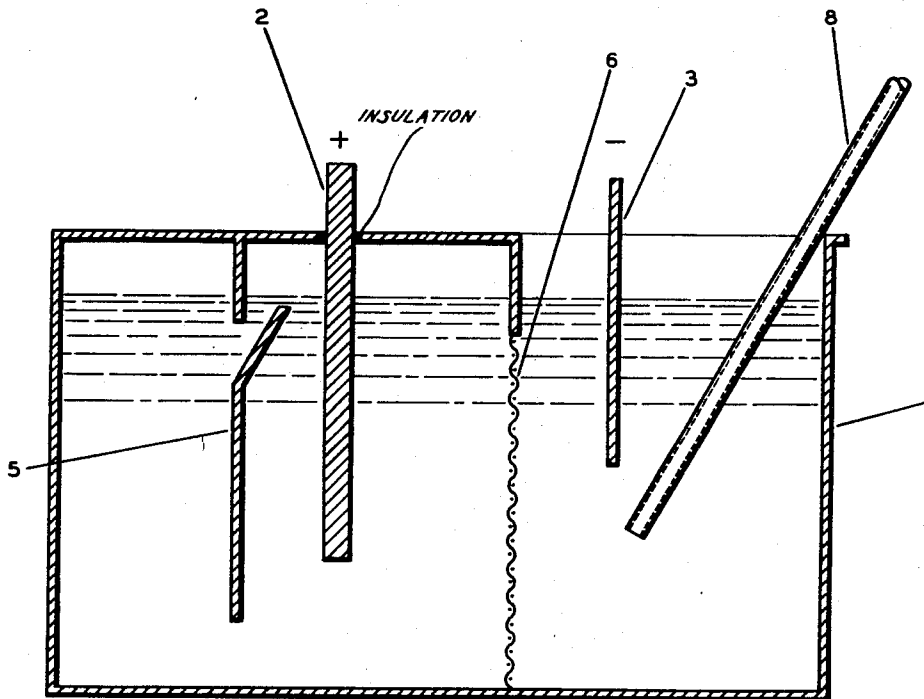
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H. N. GILBERT

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METAL CLEANING

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INVENTOR.
HARVEY N. GILBERT
BY *Harvey N. Gilbert*
ATTORNEY

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METAL CLEANING

Harvey N. Gilbert, Niagara Falls, N. Y., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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This invention relates to cleaning metals, and more particularly, to a fused bath cleaning process for removing oxide coatings from metallic articles.

Heretofore various methods have been proposed for cleaning metal articles by contacting them with molten alkali metal hydroxide compositions. In some proposed methods, the article to be cleaned is made an electrode while the alkali metal hydroxide molten bath is electrolyzed. In such processes the article to be cleaned is usually made the cathode while steel, carbon or any other material which will not react appreciably with the molten hydroxide electrolyte is utilized as anode. In such processes utilizing molten caustic baths difficulties are often encountered due to excessive corrosion of metal parts in contact with the bath. Generally such corrosion in excess is especially troublesome in regard to deterioration of the container, which usually is a steel tank. Also in some cases difficulty has been encountered with the formation of excessive amounts of insoluble material in the bath, which tends to settle out and form a sludge on the bottom of the container which appears with bottom firing methods of heating the container.

An object of the present invention is to provide a new and improved process for cleaning steel and other metal articles by means of molten alkali metal hydroxide compositions. Another object is to prevent or inhibit excessive corrosion in the use of alkali metal hydroxides for cleaning metal articles. A further object is to decrease or inhibit formation of insoluble materials in such hydroxide cleaning baths. Still further objects will be apparent from the following description of my invention.

The above objects may be attained in accordance with the present invention by the introduction of alkali metal hydride in the fused alkali metal hydroxide cleaning bath. The introduction of the hydride may be accomplished in various ways. I may add the hydride to the bath in any desired manner or I may react hydrogen with an alkali metal which has been added to the bath or which is formed in the bath, so as to form the alkali metal hydride in situ. In a preferred method, I take advantage of the fact that the electrolysis of fused alkali metal hydroxide causes the liberation of alkali metal at the cathode and I introduce hydrogen into the bath, especially in the vicinity of the cathode, so that it may react with the liberated metal to form the hydride. In such cases I prefer to operate the bath at a sufficient cathodic current

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density so that the amount of alkali metal liberated is in excess of that required to react with the oxide coating which may be on the cathode and with any moisture which may be present in the bath.

In another method I may float a layer of metallic sodium on the surface of the electrolytic bath and bubble hydrogen under the surface of the sodium so as to form sodium hydride which dissolves in the bath. Preferably, the sodium is floated on an area confined by means of a suitable submerged partition at a location in the vicinity of the work which is undergoing cathodic treatment. In another modification, I may form the hydride by reacting hydrogen with sodium floating on a bath of fused alkali metal hydroxide in a separate container and flow the solution of hydride thus formed into the metal cleaning container, preferably directing the flow by means of a suitable conduit to a point close to the work undergoing cathodic treatment.

I have found that the addition of hydride to the above-described alkali metal hydroxide cleaning bath markedly decreases the amount and extent of corrosion of iron, steel or other metals treated therein. It also markedly inhibits the formation of solid materials and I have found that when sufficient hydride is added to the bath, the formation of solid material in the bath is often completely prevented. Also, the hydride is an active deoxidizing agent and acts to reduce oxide scale on the work undergoing treatment. The hydride in solution in the bath thus supplements the cathodic cleaning action. This is especially useful in cases where complete cleaning by means of the electrolytic action alone is difficult, e. g. in cleaning coils of wire or other deeply recessed articles where the equal distribution of the electric current is difficult and in cleaning articles of relatively low electrical conductivity. In such cases the hydride, dissolved in the bath, diffuses into all recesses and insures uniform cleaning action.

While I prefer to utilize molten sodium hydroxide as the electrolyte, the other alkali metal hydroxides may be used with satisfactory results, or I may use mixtures of the alkali metal hydroxides. Likewise when operating by adding preformed hydride, any of the alkali metal hydrides may be used, but I prefer to use sodium hydride. The sodium compounds produce satisfactory results and are much cheaper than the corresponding compounds of potassium, lithium, cesium and rubidium.

I may, however, use a mixture of different al-

kali metal hydroxides to modify the melting point of the bath, e. g. mixtures of sodium and potassium hydroxides. Also, other alkali metal compounds, e. g. halides and carbonates may be added to modify the melting point. In normal operation, more or less carbonate may be present because of reaction of the hydroxide with atmospheric carbon dioxide, or occurring as impurity in technical grades of caustic soda. Such carbonate impurity does not appreciably affect satisfactory operation.

Generally I maintain the temperature of the molten electrolyte within the range of 300 to 600° C., preferably at 350 to 500° C. Still lower temperatures, e. g. as low as around 250° C. may be used by selecting mixtures having sufficiently low melting points. It is, of course, essential that the bath temperature be above the bath melting point. Temperatures above 600° C. should be avoided, in order to prevent undue decomposition of the alkali metal hydride.

The concentration of alkali metal hydride in the bath should be maintained at not less than about 0.5% by weight in the vicinity of the cathodically treated work to reap the benefits of this reagent; I prefer to maintain this hydride concentration at about 1 to 2% by weight. Still higher concentrations may be used if desired, with good results, e. g. 5 to 10% by weight.

In practicing my invention it is generally preferred to confine the hydride to the vicinity of the cathode which consists of the work undergoing cathodic treatment. In any event, I prefer insofar as possible to avoid or to minimize contact of the hydride with the anode so as to avoid loss of hydride by anodic oxidation or by reaction with the oxygen and water which are released at the anode. This may conveniently be accomplished by various modes of construction which will be apparent to those familiar with electrolytic cells. For example, I may utilize baffles or diaphragms which confine or direct the hydride or flow of hydrogen gas towards the cathode and away from the anode. I generally prefer to separate the anode and cathode by a suitable diaphragm adapted to direct the anodically formed oxygen out of the apparatus without contact with the cathode.

When molten alkali metal hydroxide is electrolyzed, the anodic products are oxygen and water. Both are deleterious if permitted to contact the cathode as they tend to react with the cathodic alkali metal, with the hydride and with the work undergoing cathodic treatment. The oxygen may be kept away from the cathode and led out of the cell by suitable well-known diaphragm or baffle means, or both. The water, however, dissolves in the molten caustic and diffuses to the cathode. This undesirable hydration of the caustic melt has always been an inevitable occurrence in the electrolysis of fused caustic, e. g. in the old Castner sodium process.

I have found that the hydration of the electrolyte in contact with the cathode can be minimized or substantially completely eliminated in my process by dissolving alkali metal oxide, e. g., sodium monoxide, in the electrolyte surrounding the anode. The monoxide rapidly reacts with the water of hydration and keeps the bath fully dehydrated, thus adding markedly to the efficiency and usefulness of my process. Sodium monoxide is soluble in molten caustic and any excess of monoxide may be converted to the hydride by reaction with hydrogen.

In a preferred modification of my invention, I

place a suitable diaphragm, for example, a sheet of steel wire gauze or other foraminous steel sheet between the anode and cathode. I then place one or more baffle means a short distance from the anode, between the anode and the adjacent side wall of the electrolyte container, adapted to cooperate with the gas-lift effect of the oxygen rising from the anode to cause bath circulation. The baffle means terminates below the surface of the bath or has one or more openings at that point, so that the electrolyte rising along the anode, after passing over the top of the baffle or through such openings, descends along the side wall. I then introduce sodium monoxide into the bath in the anode compartment, preferably into the descending stream of the circulating electrolyte. The best results are secured by continuously flowing in finely divided, solid sodium monoxide at a rate substantially equal to that required to react with the water formed by the electrolysis. At the same time, I continuously flow hydrogen into the bath in the cathode compartment, i. e., on the cathode side of the diaphragm. Preferably, the hydrogen gas is led in through one or more pipes at a point or points below the cathode or cathodes in the cell, so that the hydrogen bubbles tend to rise around the cathodic surfaces.

An apparatus suitable for use in carrying out the above-described preferred modification of my invention is shown in the accompanying drawing which illustrates diagrammatically in vertical section, the arrangement of a typical bath for use in removing oxide from ferrous metal articles.

In this drawing, 1 represents a tank constructed of steel or other suitable material. Suitable heating means (not shown) are also provided. A steel anode is shown at 2 while 3 is a cathode comprising work to be treated. In this instance, the cathode is shown as a steel bar. Baffle 5 is constructed of steel and so arranged as to cooperate with the gas-lift effect of oxygen rising from the anode and assist bath circulation. A steel wire gauze diaphragm, 6, is arranged between the anode and cathode and serves to prevent the passage of gaseous products while permitting circulation of molten electrolyte between the anode and cathode compartments. 8 illustrates an inlet pipe for the introduction of hydrogen into the cathode compartment.

In this mode of operation, any excess monoxide in solution will react with the hydrogen in the cathode compartment to form hydride. The hydrogen also reacts with sodium liberated at the cathode. The monoxide addition maintains the caustic substantially anhydrous at all times. This dehydration approximately doubles the electrical efficiency, as it avoids any substantial loss of sodium metal by reaction with water.

While my invention is of particular importance with regard to descaling iron and steel articles, the invention is not restricted thereto but is also applicable to the removal of surface oxides from various non-ferrous metals which are compatible with fused alkali metal hydroxide baths, for example nickel, silver, copper and their alloys.

I claim:

1. The process for removing oxide from the surface of a metal article compatible with fused alkali metal hydroxide which comprises electrolyzing a bath of fused alkali metal hydroxide with said article as cathode, separating the anode and cathode with a diaphragm, dissolving and maintaining 0.5 per cent to 10 per cent by weight of alkali metal hydride in said bath in the vicinity

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of the cathode, and dissolving alkali metal monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

2. The process for removing oxide from the surface of a steel article which comprises electrolyzing a bath of fused sodium hydroxide with said article as cathode, separating the anode and cathode with a diaphragm, dissolving and maintaining 0.5 per cent to 10 per cent by weight of sodium hydride in said bath in the vicinity of the cathode, and dissolving sodium monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

3. The process for removing oxide from the surface of a metal article compatible with fused alkali metal hydroxide which comprises electrolyzing a bath of fused alkali metal hydroxide with said article as cathode, separating the anode and cathode with a diaphragm, dissolving 0.5 per cent to 10 per cent by weight of alkali metal hydride in said bath in the vicinity of the cathode, bubbling hydrogen into said bath in the vicinity of the cathode sufficient to maintain a concentration of said hydride 0.5% to 10% by weight and dissolving alkali metal monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

4. The process for removing oxide from the surface of a metal article compatible with fused alkali metal hydroxide which comprises electrolyzing a bath of fused alkali metal hydroxide with said article as cathode, separating the anode and cathode with a diaphragm, dissolving 0.5 per cent to 10 per cent by weight of alkali metal hydride in said bath in the vicinity of the cathode, floating a layer of alkali metal on said bath in the vicinity of the cathode, bubbling hydrogen into said bath in the vicinity of the cathode at a rate sufficient to maintain a concentration of said hydride 0.5% to 10% by weight and dissolving alkali metal monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

5. The process for removing oxide from the surface of a metal article compatible with fused alkali metal hydroxide which comprises electrolyzing a bath of fused alkali metal hydroxide with said article as cathode, separating the anode and cathode with a diaphragm, dissolving 0.5 per cent to 10 per cent by weight of preformed alkali metal hydride in said bath in the vicinity of the

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cathode, bubbling hydrogen into said bath in the vicinity of the cathode at a rate sufficient to maintain a concentration of said hydride 0.5% to 10% by weight and dissolving alkali metal monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

6. The process for removing oxide from the surface of a steel article which comprises electrolyzing a bath of fused sodium hydroxide at a temperature of 300° to 600° C. with said article as cathode, separating the anode and cathode with a diaphragm, dissolving and maintaining 0.5 per cent to 10 per cent by weight of sodium hydride in said bath in the vicinity of the cathode, and dissolving sodium monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

7. The process for removing oxide from the surface of a steel article which comprises electrolyzing a bath of fused sodium hydroxide at 350° to 500° C. with said article as cathode, separating the anode and cathode with a diaphragm, dissolving 1 per cent to 2 per cent by weight of sodium hydride in said bath in the vicinity of the cathode, bubbling hydrogen into said bath in the vicinity of the cathode at a rate sufficient to maintain a concentration of said hydride of 1 per cent to 2 per cent by weight and dissolving sodium monoxide in said bath in the vicinity of the anode and maintaining said monoxide in an amount at least sufficient to react with all of the water formed at the anode.

HARVEY N. GILBERT.

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