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# UNITED STATES PATENT OFFICE

2,353,026

## METAL-CLEANING PROCESS AND COMPOSITION

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No Drawing. Application October 18, 1941, Serial No. 415,637

8 Claims. (Cl. 134—29)

This invention relates to the art of cleaning metals and more particularly to a method for cleaning metals in fused baths.

Oxide scale and other surface impurities are commonly removed from steel and other metal articles by treatments in aqueous solutions of acids or alkalies, with and without the utilization of electric current. A great variety of such cleaning solutions and processes are known and used for treating different kinds of metal articles and for different purposes. A common difficulty with many cleaning processes is that more or less of the base metal is removed by the cleaning operation, whereas only the surface impurities are desired to be removed.

In cleaning ferrous metals prior to electroplating, trouble is often encountered by reason of the failure of the conventional baths to remove carbon. For example when high-carbon steel is pickled with acid, a layer of carbon is left on the steel which is difficult to remove and necessitates a second cleaning operation. Because of its high carbon content, cast iron is particularly difficult to clean for electroplating, and heretofore there has been no satisfactory method for removing carbon from the surface of cast iron to leave a clean iron surface suitable for electroplating.

In some cases difficulties are encountered because of the chemically resistant nature of the surface impurities to be removed and in such cases it is often necessary to use drastic chemical treatments which not only remove the surface impurities but also dissolve a considerable portion of the underlying metal. This difficulty is encountered for example in the treatment of certain chrome alloy steels. In order to properly clean such steels for certain purposes and to remove mill scale, and the like therefrom, it is often necessary to use a drastic treatment which removes a considerable portion of the alloy steel surface. Because of the expensive nature of many of these alloy steels a process has been desired which would readily remove the mill scale and other surface impurities without substantial attack on the underlying metal surface.

An object of the present invention is to provide an improved method for cleaning metal surfaces, particularly a method which will adequately remove surface impurities without substantial attack on the underlying metal. A further object is to provide a method for cleaning ferrous metal surfaces which effectively removes carbon, particularly a method adapted for cleaning cast iron for electroplating. Another object is to provide a fused alkali bath which is suitable for cleaning steel articles without substantial attack on the steel. Further objects will be apparent from the following description of my invention.

I have discovered that the above objects may be attained by treating metals in a fused bath composed of molten alkali metal hydroxide having dissolved therein an alkali metal amide, for example, sodamide. At the temperatures common in such fused baths, for example from 350–500° C., I have found that the dissolved alkali metal amide very rapidly reacts with any carbon on the surface of the metal treated, while there is no indication of any appreciable attack on the underlying metal. In particular, I have discovered that when cast iron is treated in the alkali amide bath, sufficient carbon is dissolved from the surface of the cast iron to leave a clean iron surface which may readily be electroplated by conventional plating processes to obtain adherent plated coatings.

In one method of practicing my invention I may first provide a fused bath comprising an alkali metal hydroxide containing in solution an appreciable quantity of an alkali metal amide. I may for example utilize a bath consisting of molten caustic soda having dissolved therein from 1–25% of sodamide ($NaNH_2$). Preferably, the bath is protected from oxidizing influences so as to prevent oxidation of the amide. A preferred method of preventing oxidation of the active ingredient of the bath is to continuously pass a stream of ammonia gas into the bath. The ammonia may or may not be preheated, as desired. The ammonia may be diluted, as desired, with other non-oxidizing or inert gases, e. g., nitrogen or hydrogen.

A convenient and preferred method of operating my process consists in floating a layer of molten sodium on the surface of a fused caustic soda bath and passing in ammonia so that it comes into contact with the sodium at the interface between the sodium and caustic layers, for example by passing the ammonia in below the surface of the caustic so that it rises through the caustic and thence into the layer of sodium. In this way the sodamide which is formed in the presence of the molten caustic soda immediately dissolves therein, forming a solution of the sodamide in the caustic soda. The layer of sodium metal protects the amide in the bath from oxidation with the air and the sodium layer may in turn be protected from oxidation if desired, for example, by maintaining over it an atmosphere of

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non-oxidizing gas. If desired, by the means of a suitable partition a small portion of the bath wherein work is to be introduced may be kept free from the sodium layer and if desired, this portion of the bath may be protected from the air by means of a non-oxidizing gas atmosphere or by the use of a floating layer of solid material insoluble in the bath, for example finely divided carbon such as charcoal or graphite. When operating with relatively low sodamide concentrations in the bath, e. g., 2 to 10% by weight, it is not always necessary to so protect the bath surface.

In another method of preparing the herein described sodamide solution, I may react ammonia with a fused mixture of alkali metal oxide and alkali metal hydroxide, for example, a mixture of sodium monoxide and sodium hydroxide. Such alkali metal oxide readily dissolves in alkali metal hydroxide and in that solution it readily reacts with ammonia to form the amide. In operating a bath prepared in this manner it is usually preferable to convert all of the alkali metal oxide to amide before treating the work therein. When the alkali amide content becomes depleted, some of the bath may be regenerated by adding more alkali metal oxide and again treating the bath with ammonia. Preferably, the treatment with ammonia is continued while the bath is being utilized to clean metal articles.

Baths suitable for my cleaning process also may be made by dissolving preformed solid alkali metal amide in the alkali metal hydroxide fused bath.

For many purposes I prefer to utilize a fused caustic bath containing alkali metal hydride in addition to alkali amide and my invention includes the use of such mixed baths. As described and claimed in my copending application Serial No. 339,919, alkali metal hydride dissolved in fused caustic rapidly reduces oxide scale to the metallic form, and hence is an excellent scale-removing agent. In some cases, the alkali metal hydride has proved to be more efficient than the amide in removing scale, but it does not have the active carbon removing property of the amide. Hence by utilizing a bath containing both the amide and hydride, I can effectively descale and remove carbon in a single operation.

I have discovered that the alkali amide and hydride are compatible in the caustic bath and may be dissolved together in the caustic in any desired amounts, up to around 25% by weight of the amide and up to around 20% by weight of the hydride. Such mixed baths may be prepared by any convenient method, for example by mixing a hydride bath with an amide bath, or by forming both the amide and the hydride in the bath. For example a preferred method is to react sodium in a caustic soda bath, as described above, with a mixture of hydrogen and ammonia or with a gas mixture containing these gases. A convenient method is to subject ammonia to a conventional catalytic cracking process, whereby a portion of the ammonia is converted to nitrogen and hydrogen, resulting in a mixture of ammonia, hydrogen and nitrogen and passing this gas mixture beneath a layer of molten sodium floating on a caustic soda bath. By suitably varying the proportions of ammonia and hydrogen in the gaseous reagent, the proportional concentrations of amide and hydride in the bath may be varied as desired. Ordinarily, in such mixed baths, I prefer to utilize concentrations of about 2 to 10% by weight of the amide and 2 to 5% by weight of the hydride.

*Example I*

A bath of fused caustic soda is dehydrated by adding sodium until gas evolution ceases. Sodamide is then added in amount sufficient to make a 5% concentration of sodamide in the fused caustic. The bath is held at a temperature of 350° C. and articles of sheet iron are immersed in the bath for five minutes. The articles are then removed from the bath and quenched by plunging them into a tank of water. The scale originally adhering to the metal is reduced by the bath but remains loosely attached to the metal surface and this reduced metal is removed when the hot metal is thrown into the water. After washing the article it is free from scale and can be subsequently treated by conventional electroplating, hot dip metal coating or enamelling processes to obtain adherent coatings.

*Example II*

A bath of fused caustic is dehydrated by adding sodium until gas evolution ceases. In an iron bell dipping beneath the surface of the caustic, a charge of sodium is floated on the molten caustic and ammonia gas is introduced into the caustic and allowed to rise to the interface of the sodium and caustic where it reacts to form sodamide. The sodamide dissolves in the fused caustic and diffuses throughout the entire caustic bath. A layer of sodium is maintained by adding sodium to the bell as required and ammonia is added in amounts necessary to build up and maintain a concentration of 6% sodamide in the bath at all times. The temperature of the bath is held at 350° C. Cast iron articles are placed in the caustic sodamide bath for ten minutes and are then removed and cooled and then washed with water. The resulting cleaned cast iron surface is substantially free from carbon and may be electroplated by conventional means to obtain electroplated coatings equal in quality to those regularly obtained on clean iron or steel surfaces.

*Example III*

A dehydrated fused caustic bath is treated with sodium and a mixture of ammonia and hydrogen in the same apparatus described in Example II and operated at a temperature of 350° to maintain a bath containing 5% sodamide and 5% sodium hydride. Cast iron pieces are treated by immersing them in this bath for ten minutes and subsequently removing them from the bath, cooling and washing. Such treated cast iron surfaces are suitable for electroplating or other processes requiring a clean metal surface.

The invention is not restricted to baths which contain only alkali metal hydroxide and alkali amide, as various fusible diluents may be added without departing from the spirit and scope of my invention. For example alkali metal halides, carbonates or other fusible inorganic compounds suitable for addition to fused salt heat treating baths which are inert to the alkali amide may be added, including fusible compounds of metals other than the alkali metals. Addition of such compounds may be made in order to obtain baths having various melting points. For example, by addition of sodium iodide to a caustic soda bath containing sodium amide, compositions may be made having low melting points, so that the baths may be operated at temperatures as low as about 250° C. Similar low melting composi-

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tions may be made by dissolving the alkali metal amide in fused mixtures of sodium and potassium hydroxides. The various diluents which can thus be added to vary the melting point of the bath will be apparent to those skilled in compounding fused baths for metal treatment. Obviously, any ingredient added to the baths must be substantially chemically inert to the alkali metal hydroxide and amide or at least if it combines with the hydroxide, it must form a fusible compound which likewise will dissolve the alkali metal amide. Also, all bath ingredients must be substantially non-oxidizing in character.

While I prefer to use sodamide and sodium hydroxide because of their cheapness and availability, the amides and hydroxide of the other alkali metals, e. g., potassium, and lithium, may be used with substantially equal effectiveness.

In most cases after treatment in the fused amide bath, it is preferable to immediately quench the treated metal articles with water, in order to obtain the best cleaning results. For example I have found that in cleaning steel the sodamide bath treatment alone does not always completely remove mill scale but reduces it to form a slightly adherent coating on the steel. When the steel articles are removed from the bath and quenched with water the reduced scale and other impurities immediately separate from the steel, leaving a clean, bright surface. The quenching with water may be accomplished either by dipping the article in a bath of water or by spraying or otherwise flowing a stream of water onto the article as desired. If the article is not heavily scaled or is free from scale, it is not necessary to quench with water. For example in treating cast iron to remove carbon, I have obtained equally good results with and without quenching. In the latter case, the treated articles were merely cooled in air, and washed with water and then were ready for electroplating.

The bath temperature for the metal cleaning operations may be varied as desired over a wide range above the melting point of the molten bath. For example, using solutions of sodamide in fused caustic soda, excellent cleaning of various metals may be accomplished at temperatures from 320 to around 600° C.

The alkali amide concentration of the cleaning bath may vary from 1 to 25% by weight, or even higher. For most purposes, I prefer to maintain a concentration of around 2 to 10% by weight of the amide. At the higher concentrations, the possibility of some loss due to oxidation is increased, especially at the higher temperatures. Ordinarily there is no necessity to exceed an alkali amide concentration of about 10% by weight, nor to operate at temperatures above 350 to 400° C.

I have utilized my cleaning process to clean various types of iron and steel, including cast irons and in each case have found the method effective to remove the commonly occurring surface impurities, leaving a clean, bright surface. Likewise, I have cleaned various non-ferrous metals and alloys, for example, copper, nickel and their alloys, nichrome and various alloys commonly used as electrical resistors. Metal surfaces so cleaned are in excellent condition for electroplating, hot dip coating, enamelling or other operations requiring a perfectly clean surface, without further treatment.

My alkali amide bath is especially useful to remove carbon from the surface of ferrous metals. For example, it effectively removes carbon from cast iron surfaces to produce a clean iron surface which can be electroplated with copper, zinc, nickel, tin and the like with excellent results. Another example is steel which has been annealed under non-oxidizing conditions. Such annealed steel often has on its surface fine carbon particles or "smut" on its surface, which is difficult to remove except by relatively expensive mechanical treatment. My herein described cleaning process rapidly removes such carbon "smut" from the steel, leaving a clean surface.

The herein described alkali amide solutions may conveniently be prepared at a distance from the place of utilization, cooled and stored and shipped in sealed containers. On cooling the composition becomes a solid solution of the alkali amide.

I claim:

1. The process for cleaning metal articles composed of metals substantially non-reactive with molten alkali metal hydroxide to remove surface impurities such as metal oxides and carbon which comprises immersing said articles in a molten composition comprising at least one alkali metal hydroxide containing about 1 to 25% by weight of dissolved alkali metal amide and then quenching said articles with water.

2. The process for cleaning ferrous metal articles to remove metal oxides which comprises immersing said articles in a molten composition comprising sodium hydroxide containing about 1 to 25% by weight of dissolved sodamide.

3. The process for cleaning metal articles composed of metals substantially non-reactive with molten alkali metal hydroxide to remove surface impurities such as metal oxides and carbon which comprises immersing said articles in a molten composition comprising at least one alkali metal hydroxide containing about 1 to 25% by weight of alkali amide and up to 20% by weight of alkali metal hydride dissolved therein.

4. The process for cleaning ferrous metal articles to remove metal oxides which comprises immersing said articles in a molten composition comprising sodium hydroxide containing about 1 to 20% by weight of sodamide and up to 20% by weight of sodium hydride dissolved therein.

5. A fused bath for cleaning metal articles composed of metals substantially non-reactive with molten alkali metal hydroxide to remove surface impurities such as metal oxides and carbon which comprises molten alkali metal hydroxide having about 1 to 25% by weight of alkali metal amide dissolved therein.

6. A fused bath for cleaning ferrous metal articles to remove metal oxides which comprises molten sodium hydroxide having about 1 to 25% by weight of sodamide dissolved therein.

7. A fused bath for cleaning ferrous metal articles to remove metal oxides which comprises molten sodium hydroxide having about 1 to 25% by weight of sodamide and about 1 to 20% by weight of sodium hydride dissolved therein.

8. A composition of matter comprising a solution of about 1 to 25% by weight of at least one alkali metal amide and up to 20% by weight of at least one alkali metal hydride in alkali metal hydroxide, which composition is a solid at atmospheric temperatures.

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CERTIFICATE OF CORRECTION.

Patent No. 2,353,026. July 4, 1944.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 49, claim 4, for "1 to 20%" read --1 to 25%--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of September, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.