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PROCESS OF CLEANING METAL SURFACES AND COMPOSITIONS THEREFOR

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2 Claims. (Cl. 134—3)

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This invention relates to a process of improving and cleaning metal surfaces, and more particularly the surfaces of ferrous metals and other alkali-resistant metals, and to compositions adapted for use in such a process. More particularly, our invention relates to a method wherein the metal is immersed in a bath comprising a molten mixture of an alkali metal nitrate and an alkali metal hydroxide, and which in its preferred form also includes a relatively small amount of an alkali metal chloride. This step removes organic impurities, and converts inorganic surface impurities, such as rust or scale, into a black oxidized coating, which is readily removed by a brief immersion in dilute acid or otherwise as set forth hereinbelow, leaving the metal surfaces bright and clean. When it is desired to resurface the metal and to obtain a uniform black oxidized finish, suitable as a base for lacquers, paints or the like, our invention further contemplates again immersing the metal in a bath comprising a molten mixture or alkali metal compounds as aforesaid.

This application is a continuation of a prior application Serial No. 431,168 of February 16, 1942, now forfeited, in turn a continuation in part of our application Serial No. 377,486, filed February 3, 1941, now abandoned.

For various purposes, as for example when metals are to be provided with coatings of various kinds, it is frequently necessary to clean the surfaces of the metal and to remove impurities ordinarily found thereon, such as oxides, scale, dirt, grease and oil. For the removal of organic matter such as grease and oil, it has been common to treat metal articles with organic grease solvents, for example liquid chlorinated hydrocarbons. For the removal of oxide impurities, such as mill scale and forging scale, and for special purposes, it has been common to immerse metal articles or to treat the metal surfaces with strong acid pickling baths, for example hot sulfuric acid. However, it has frequently been necessary to select particular acids for particular types of inorganic surface impurities to be removed. Because of the selective dissolving nature of the solvents heretofore used, it has frequently been necessary to employ more than one type of solvent, often in a series of treatments. This practice is time-consuming and expensive and leaves much to be desired.

Thus, the acid pickling process requires a long time for the removal of all the scale from ferrous metals. It has the additional disadvantage that it tends to cause "hydrogen embrittlement"

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of the metal. Other problems incident to acid pickling reside in the disposal of the waste liquor and in the fact that vapors having a deleterious effect on the health of the workmen are usually liberated from the bath. In many cases it is difficult to control the action of the acid on the metal surfaces in such a manner as to avoid undesirable action of the acid on the true metal surface after the impurities have been dissolved and removed. Attempts have been made to solve this problem by adding corrosion inhibitors to the acid, but such inhibitors add to the expense and have not proved completely successful from all standpoints. Consequently, in acid pickling operations, the acid usually does attack the metal surface to some extent, causing loss of metal, diminution in the strength of the acid, and uneven cleaning. Metal surfaces cleaned in acid pickling baths frequently exhibit a surface phenomenon commonly known as "pickle smudge." Metal surfaces in which "pickle smudge" is evidenced are usually difficult to plate; this phenomenon makes the application of uniform protective coatings difficult or impossible.

Mechanical removal of surface impurities from metals by sand-blasting and similar abrasion methods is also used to some extent, but requires expensive equipment and elaborate protection for the workmen.

Among the objects achieved by our invention is the provision of a process of improving the surfaces of alkali-resistant metal articles, whereby such surfaces may be rendered clean and bright, or provided with an advantageous protective coating in a simple and efficient manner and without encountering difficulties or disadvantages inherent in prior art methods.

A further object achieved by our invention is the provision of novel compositions of matter useful for forming metal-treating baths for use of a process as set forth above.

Our invention has, for further objects, such additional operative advantages and improvements as may be found to obtain hereinbelow.

We have found that organic surface impurities ordinarily found on alkali-resistant metals (including alkali-resistant metal alloys) can be removed, and inorganic surface impurities transformed into compounds easy to remove in a simple and inexpensive manner, by immersing the metal in a bath comprising a molten mixture of an alkali metal nitrate and an alkali metal hydroxide, and preferably also containing a small amount of an alkali metal chloride. In this treatment, organic impurities are completely de-

stroyed or removed, and inorganic surface impurities are converted to a black oxidized coating. This oxidized coating may readily be removed in a simple manner, as for example by immersion in dilute mineral acid, such as dilute hydrochloric or sulfuric acid, of such character as will not in itself tend to leave an insoluble residue on the metal surfaces, or in some cases by immersion in a bath comprising a molten mixture of an alkali metal hydroxide and an alkali metal chloride. Thus, a dilute hydrochloric acid bath quickly removes the black oxide coating, leaving the surfaces of the metal bright and clean. In the case of Monel metal, stainless steel, and other rust-proof alloys, the metal so cleaned is satisfactory without further treatment for applications where an ornamental, highly finished surface is required, as for example in the manufacture of tableware, cutlery, or the like from stainless steel.

In some cases, as for example where the amount of inorganic surface impurity on the metal is small, or where it is not intended to apply a paint or lacquer, the initial molten bath immersion is sufficient. But when the original surface deposits are large or irregular, or where an exceptionally smooth protected surface is desired, as a base for lacquering or the like, we have found it desirable to first immerse the metal in a molten caustic-nitrate bath as aforesaid, followed by immersion in dilute acid, preferably with an intermediate water rinse, whereby the surfaces of the metal are made bright and clean, and then to immerse the metal again in a molten salt bath of the general character indicated above, in order to obtain an exceptionally pure, smooth and uniform oxidized coating, especially suitable as a paint, varnish or lacquer base.

Our invention contemplates the use of the compounds (hydroxide, nitrate and chloride) of any of the alkali metals, such as potassium, sodium or lithium, but we usually employ the sodium compounds on account of their relatively low cost.

Preferably, the molten bath should contain a relatively large amount of the alkali metal hydroxide, that is to say from 1.5 to 3.0 parts by weight, per 1 part by weight of alkali metal nitrate. In many instances, the bath may consist of these ingredients alone, but we have found that the activity of such a bath may be increased, and the time of treatment shortened, by including a relatively small amount of an alkali metal chloride, as for example from 0.1 to 0.5 part by weight, per 1 part by weight of the nitrate. Where the metal is first immersed in the molten bath, followed by immersion in dilute mineral acid and a second immersion in a molten bath, the bath used for the first treatment preferably contains a small amount of alkali metal chloride, as disclosed above, but the bath used for the second treatment may either be the same bath used in the first treatment, or a fresh bath comprising a molten mixture of alkali metal hydroxide and alkali metal nitrate, with or without alkali metal chloride.

On the other hand, when the purpose of the second bath is to remove the oxidized coating formed in the initial immersion, the nitrate is omitted; in this instance the second bath will comprise largely alkali metal hydroxide in admixture with a minor amount of alkali metal chloride.

An advantageous mixture, which we have found useful for many applications, may be prepared by

mixing 2 parts by weight of sodium hydroxide, 1 part by weight of sodium nitrate and from 0.1 to 0.5 part by weight of sodium chloride. Such a composition, containing about 0.35 part of sodium chloride, has a melting point of approximately 500° F., a heat of fusion of 49.6 cal./gm. and a specific heat of 0.230 cal./gm./°C. While the ingredients may be mixed in the cold and the mixture melted when it is desired to use it, we have found it desirable, when marketing such a composition, to melt the ingredients together, after which the fused mass may be poured into suitable molds or drums for shipping, to be remelted at the point of use.

In use, the mixture is placed in an ordinary iron pot or other alkali-resistant container, and heated in any suitable manner until melted. When the composition has been melted and the temperature of the bath is within the operating range, the articles to be cleaned are immersed in the bath for a predetermined period of time, usually from 2 to 5 minutes, and they are then withdrawn and dipped in water or sprayed to remove entrained salts. It is advisable to thoroughly dry the metal before treatment in order to avoid any spattering of molten salt.

The time required to effect treatment in accordance with our invention will, of course, vary with the amount of impurities, the size and weight of the articles to be treated and the type of materials to be cleaned and will ordinarily run from 15 seconds to 30 minutes. Often it is only necessary to leave the articles in the bath for a period of time sufficient to bring them to the temperature of the bath.

The minimum temperature of treatment is that necessary to maintain the bath in a molten condition, but a somewhat higher temperature ordinarily does no harm. By way of example, the specific mixture referred to above works best within a temperature range of from 550° to 650° F.

The metal surfaces, subsequent to the initial treatment, have a dull black finish. The organic impurities have been oxidized and removed, and the inorganic impurities have been oxidized and removed, and the inorganic impurities have been transformed into oxidation products readily removable by means of a dilute acid treatment or other suitable treatment. These oxidation products form a black coating on the surface of the metal, the uniformity of which will depend to a considerable extent upon the character and amount of the original surface impurities. A portion of the oxide coating is undoubtedly formed by oxidation of the metal itself, but the action is uniform and confined to the surface, and metal losses are negligible. Where a bright metallic surface is desired, as is usually the case when the metal is to be plated or placed in a hot lead dip, and where hydrogen embrittlement is not a serious factor, the black oxide coating is advantageously removed by a brief immersion in dilute hydrochloric or sulfuric acid. The commercial dilute acids may be used for this purpose, at atmospherc temperature, the time of immersion ordinarily being limited to a few seconds.

In some cases, however, as for example in treating spring steel alloys, even a slight degree of hydrogen embrittlement is a serious factor, and it is important to avoid any treatment with acid. In such cases, we have found that, following the initial immersion, the oxide coating left by such immersion can be removed by immersing the

metal in a bath composed of a major amount of sodium hydroxide and a small amount of sodium chloride, but containing no sodium nitrate or other oxidizing agent. By operating in this manner, the oxide coating is removed, leaving a clean metal surface and without impairing the properties of the metal itself.

By way of specific example of our invention, various metal articles covered with mill scale were immersed in a hot molten bath consisting of 1 part by weight sodium nitrate, 2 parts by weight sodium hydroxide and 0.25 part by weight sodium chloride, and held in the bath at approximately 600° F. for 5 minutes. When removed and rinsed, the surfaces of the metal parts exhibited a dull black finish. After immersion of the treated parts in a bath containing between 8 per cent to 10 per cent HCl for 15 seconds, the metal parts exhibited surfaces having a bright metallic finish, free of scale. These parts were found to be well suited for electroplating or hot lead dipping. By reimmersing some of the parts so treated in the original molten salt bath, they were provided with a smooth black resistant coating forming an advantageous base for lacquering, painting or the like.

In another specific example of our invention, we applied our process to certain cast iron parts, for the purpose of preparing them for hot lead dipping. These parts presented a difficult problem, having surfaces with considerable rust and scale deposits, as well as considerable amounts of adherent or imbedded silica. So far as we are aware, no prior methods are fully satisfactory when attempting to prepare such material for hot lead dipping. Thus, we found that prolonged immersion of specimens of these parts in hydrofluoric acid failed to give surfaces suitable for hot lead dipping; it was impossible to obtain lead coatings free from pin-holes or pores of such character as to form foci for corrosion or oxidation.

Because of the extraordinarily difficult character of the problem, we first immersed these cast iron parts in 20 per cent H_2SO_4 for from 3 to 5 minutes, at about 180° F. This preliminary pickling is not usually necessary, but helps, in aggravated cases, to somewhat loosen the surface impurities and to render them easier to oxidize. However, neither this pre-treatment nor prolonged pickling proved adequate for the purpose stated.

The parts were then removed from the acid bath, rinsed and dried, and then immersed in a molten bath of the same composition as that used in the preceding example. They were maintained in the molten bath at approximately 600° F. for about five minutes, then removed, rinsed, immersed in 20 per cent HCl for about one minute, and then rinsed and dried. Specimen parts, so treated, were dipped in hot lead, thereby acquiring a uniform lead coating free from pinholes and otherwise satisfactory in character. By contrast, prior art difficulties in obtaining satisfactory results on articles of this kind demonstrate and emphasize the value of our invention, in this aspect thereof.

Baths prepared in accordance with our invention may be used for extended periods of time without material deterioration. They are suitable for use in cleaning all of the common commercial alkali-resistant metals such as cast iron, stainless steel and other ferrous metals and alloys, brass, copper and copper alloys, Monel metal and the like. They are not suitable for treating

zinc, aluminum or magnesium, that is to say, metals and alloys readily attacked by alkalies.

Our process is simple and inexpensive and may be carried out in inexpensive apparatus by ordinary labor without the use of skilled help, representing a marked saving over prior art processes. No noxious vapors are given off by the bath, and the spent mixture when cooled is a solid and readily disposable. The process exhibits a selective action on surface impurities, and does not cause corrosion, substantial loss of weight, or hydrogen embrittlement. The surfaces of the metal after treatment are either bright and clean, free from "pickle smudge" or the like, or provided with a uniform oxidized coating, depending upon the type of treatment employed.

Our process, which as aforesaid utilizes a mixture of solid alkali metal nitrate and hydroxide, and preferably chloride, at the high temperatures necessary to maintain such a mixture in a molten condition, is sharply distinguished from prior methods employing solutions of similar compounds, even at the high concentrations. Such aqueous solutions tend, for example, to remove organic impurities by emulsification or saponification, whereas in our process the high temperature and the powerful action of the molten bath appear to completely oxidize and destroy organic impurities. The action of our process upon inorganic impurities is also more drastic and effective than when aqueous solutions are employed.

So far as we have been able to determine, molten mixtures of alkalies and other oxidizing agents are far less effective and desirable; we have not found any other oxidizing agent which can be used to replace the alkali metal nitrate with equally good or even comparable results.

While we have described our invention hereinabove with respect to various specific examples and operating details, it will be obvious to those skilled in the art that our invention is not limited to such details and examples, but may be variously practiced and embodied within the scope of the claims hereinafter made.

We claim:

1. A two step non-electrolytic process for cleaning the surfaces of alkali resistant metals, wherein each step is in the nature of a chemical reaction, and wherein the second step leaves no added finish to the surface, and wherein the first step comprises immersing the metal in a bath comprising a molten mixture of one part by weight of alkali metal nitrate and from 1.5–3.0 parts by weight of alkali metal hydroxide, and from 0.1–0.5 part by weight of alkali metal chloride, for a period of time sufficient to remove any organic surface impurities and convert inorganic surface impurities to an oxidized coating, more readily soluble than were the original inorganic impurities, the operating temperature of the first bath being above the melting point of the molten mixture, and wherein the second step comprises immersing the metal in a bath of a dilute acid selected from the class consisting of hydrochloric and sulphuric acids, whereby when the metal is immersed therein for a proper period of time, the bath will react chemically with the oxidized coating to remove it, so as to leave the surface free of the original impurities and of the oxidized coating as well, the second step, however, being such as not to expose at the surface other impurities, not previously existent, or not previously exposed, thus leaving the surface free of all impurities and consisting solely of the metal, the immersion in the second bath being sufficiently brief so as not

to permit the acid to attack the metal, but merely to remove the oxidized coating formed by the first step.

2. A descaling composition for alkali resistant metals for use in molten bath form consisting essentially of a mixture of one part by weight of alkali metal nitrate, 1.5–3.0 parts by weight of alkali metal hydroxide, and 0.1–0.5 part by weight of alkali metal chloride.

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