

1

3,260,619

METHODS AND COMPOSITIONS FOR CLEANING METAL

Robert H. Shoemaker and Harold Geschwender, Detroit,
Mich., assignors to Kolene Corporation, Detroit, Mich.
No Drawing. Filed Feb. 4, 1965, Ser. No. 430,465
14 Claims. (Cl. 134—3)

This is a continuation-in-part of our earlier application of the same title, Serial No. 241,169, filed November 30, 1962, now abandoned.

This application relates to methods and compositions for cleaning metal and relates more particularly to the cleaning of a large variety of normally difficult metal surfaces.

As conducive to a better understanding of the instant inventive concept, it should be recognized that various materials in the form of fused molten alkali salts have been used heretofore for removing oxide scale and the like from metal surfaces, such as the well known mixture disclosed in Webster et al. U.S. Patent No. 2,458,661 known in the trade as Kolene K-1. While such materials are extremely efficient for many applications, it has been found that, with certain particularly difficult problems, prior art compositions and methods are somewhat lacking. For example, stainless steel tubing and the like is frequently manufactured by an extrusion or drawing process utilizing glass of various forms as a lubricant. Such procedures are described in detail in Sejourne et al. Patent No. 2,538,917 among others. The resulting product not only has an oxide scale formed on its surface from the high temperatures utilized, both on its interior and exterior in the case of tubing, but further includes a tenaciously bonded, fused, vitreous coating which is frequently uneven, ranging in thickness from a few thousandths of an inch to as much as 1/4 inch in places. Many mechanical means such as sandblasting and the like are used industrially for the removal of this coating, but it will be readily seen that, in addition to the inherent difficulties of such a procedure, the stainless steel surface resulting therefrom may well be pitted or otherwise marred. Although certain molten alkali baths such as K-1 are useful in the cleaning of surfaces subjected to this type of treatment, it may be necessary to immerse the metallic product from six to eight times before all of the glass and oxide is removed. This "thus-formed" glass coating has been found more difficult to clean than siliceous materials resulting from casting molds or other investment procedures.

In addition to the cleaning of glass-coated metals resulting from Sejourne and other like processes, various other difficult problems have been encountered utilizing prior art materials. For example, the removal of scale from titanium, while possible with compositions currently in use, presents unique problems in that at the elevated temperatures of 900° F. and above necessary for efficient cleaning heretofore, the metallic surface has a tendency to pick up hydrogen resulting in a phenomenon known as hydrogen embrittlement which detrimentally affects the properties of the metal thereby necessitating the use of a vacuum annealing. Prior art materials have been tried at temperatures below 900° F., but at these relatively low treating temperatures, in addition to a substantial decrease in the cleaning effectiveness of the salts, the molten bath has become extremely viscous rendering the same particularly difficult to desludge. In order to provide a commercially feasible metal cleaning procedure, it is desirable to utilize a molten salt bath of a relatively low viscosity which is capable of having the sludge, in the form of oxides and the like removed from the metal surfaces, continuously displaced by agitation or the like

2

in a manner such as disclosed, for example, in Shoemaker et al. U.S. Patent No. 2,863,465 whereby the effectiveness of the bath will be realized for an extended period of time whether the cleaning operation is of the batch, or continuous, type. Prior art materials have been particularly inefficient, both from a cleaning and from a desludging standpoint, unless the relatively high temperatures mentioned hereinabove were utilized. These problems are somewhat magnified with the use of various alloys of titanium which are more difficult to descale than pure titanium and with which it has been necessary to use temperatures substantially in excess of 900° F., and sometimes even above 1000° F. in order to provide complete descaling.

Similarly, many of the highly sophisticated alloys known generally in the trade as "superalloys" or wrought heat-resisting alloys are particularly difficult to clean utilizing prior art materials. Such alloys have high oxidative resistance and tensile strength at temperatures up to about 2500° F. and contain additives such as chromium to combat oxidation, nickel, manganese, nitrogen, molybdenum or tungsten to render the same "austenitic" and cobalt, titanium, aluminum and silicon to further provide superstrength and other desirable characteristics for use in high pressure industrial equipment, jet-engines, missiles and the like. Once again, the use of normal temperature ranges in excess of 900° F. necessary with prior art materials produces a product having many deficiencies. For example, superalloys descaled in this manner are subject to pitting, possible galvanic attack in the salt, particularly with molybdenum-bearing alloys, and possible age hardening. Further, prior art compositions at these high temperatures have a tendency to form more oxides on the metallic surfaces than they remove as contrasted with the reverse in the instant case. Attempts to use lower temperatures with these superalloys result in inefficient descaling and undue viscosity of the molten bath rendering the same difficult to desludge.

It is a primary object of the instant invention to provide compositions and methods for the cleaning of various metals which are free from the foregoing, and other, disadvantages.

Another object of this invention is the provision of fused, substantially anhydrous, molten alkali salt mixture which is particularly adapted for exceptionally difficult cleaning processes.

A further objective of the instant invention is to provide a material of the type described having a composition uniquely capable of use in a large variety of different procedures without modification.

A particularly important object of this invention is the provision of a composition having the ability to efficiently clean particularly sensitive metallic surfaces at relatively low temperatures, for example, below 900° F., and preferably below 800° F., without becoming undesirably viscous and difficult to desludge.

Yet another object of the instant invention is to provide a method for both descaling and deglassing materials manufactured utilizing a vitreous lubricant at high temperatures.

A further object of this invention is the provision of methods for descaling titanium and alloys containing a predominant portion of titanium which preclude hydrogen pickup thereby avoiding the necessity of relatively expensive protective treatments such as vacuum annealing.

A still further object of this invention is the provision of methods for cleaning the surfaces of wrought heat-resisting steel alloys in such a manner as to preclude deleterious effect on the characteristics of the product.

Additionally, it is an important object of this invention to provide a composition and methods for the cleaning of metals which are highly efficient and reliable in operation,

relatively inexpensive and simple in practice, and particularly noncorrosive to the equipment being utilized.

Other and further objects reside in the particular combination and quantitative ratios of the component parts of the compositions and the specific arrangement of the manipulative steps of the methods.

Consistent with the above objectives, it has been found that a fused, substantially anhydrous cleaning material formed of the following mixture has all of the desired properties and characteristics:

Material	Range, weight per cent	Preferred, weight per cent
Sodium nitrate.....	9-15	12
Sodium chloride.....	5-15	10
Potassium hydroxide.....	8-20	15
Sodium hydroxide.....	50-78	63

Of particular importance in the formation of the compositions to be utilized according to the methods of the instant invention is the weight ratio of potassium hydroxide to sodium hydroxide. While many prior art patents generally suggest the use of one or both materials, it has not been recognized heretofore that the potassium hydroxide provides unique advantages to the composition. Potassium hydroxide is more aggressive and dissolves the iron in iron oxide scales more readily than sodium hydroxide baths. Similar compositions without the potassium hydroxide have been found to be particularly inefficient and undesirable in that they fail to provide the excellent descaling and deglassing properties of the material of the instant invention and further in that they are found to sometimes even oxidize the metallic surface being treated rather than remove the oxides. A weight ratio between these constituents of at least 0.1 has been ascertained to be necessary to render the composition effective as a multipurpose cleaning material and particularly with regard to its efficiency in the descaling of titanium and certain difficult titanium alloys. Further, the presence of the potassium hydroxide in at least this quantitative ratio has provided the unique descaling-deglassing properties for cleaning metal surfaces manufactured utilizing a vitreous lubricant. Also, the maintenance of this potassium hydroxide level renders the material especially effective for cleaning other normally difficult metallic surfaces such as those of wrought heat-resisting steel superalloys. The upper level of the weight ratio between potassium hydroxide and sodium hydroxide in the composition may be somewhat varied, but it has been found that a value of substantially in excess of 0.4 is undesirable from a commercial viewpoint. The advantageous cleaning properties provided by the presence of the potassium hydroxide must be balanced against its increased cost as compared with sodium hydroxide and its corrosive effect on both the equipment being utilized and the material being treated.

The presence of the sodium nitrate in the molten alkali bath has also been found to be critical to the production of an efficient descaling and/or deglassing technique. This material in the specific mixture defined hereinabove contributes to the unique properties of the bath and its capability of use for many varied cleaning purposes.

It will be noted that the sodium chloride is included in a relatively high percentage as compared to the one or two percent sodium chloride remaining in commercially produced caustic from its manufacturing process. This material assists in providing a molten bath which remains relatively thin or of low viscosity even at somewhat reduced treating temperatures such as below 900° F. or even below 800° F. As pointed out hereinabove, this property of the molten bath of this invention is extremely important in order to provide a commercially acceptable method of continuously desludging the same thereby extending its effective life and precluding undesirable contamination of the product.

Although each of the materials forming part of the bath of this invention are known in and of themselves for use in the cleaning of metallic surfaces, the particular combination defined hereby and the specific quantitative relationship between the components of the mixture, provide a synergistic result not realizable from the individual materials or other combinations of the same. Specifically, this particular composition has the advantage of being useful without modification for cleaning in an efficient manner various metallic surfaces which have caused difficulty in the past.

While it is particularly important to include all of the materials in the quantitative ratios set forth hereinabove, it is also of great importance to exclude various materials found in previously known compositions. For example, certain baths suggested by the prior art have required the presence of additional components such as alkali carbonates. However, it has been found that baths of this composition must be frequently replaced because their effectiveness has deteriorated below a point of minimum usefulness. This relatively rapid decrease in efficiency of the bath is a direct result of the presence of the carbonate. Similarly, the inclusion of various other materials has been found to produce deleterious effects on the bath in many instances. Hydrogen-containing compounds, such as hydrides and the like, render the bath undesirable for titanium cleaning in that the effects of hydrogen embrittlement are increased. Thus, the specific composition defined by this invention, and this composition alone, can provide the unique multipurpose characteristics desired.

With regard to the treating methods, the metal to be cleaned is immersed in a molten bath of the above composition for a period of time which may be as little as 30 seconds while the bath is maintained at an elevated temperature. It will be understood that the time of the treatment will depend upon the size of the work-piece as well as the type and thickness of the material to be removed and the temperature of the bath. While the temperature may vary over a substantial range of from above its melting point to in excess of 1000° F., the specific composition of the bath of this invention allows the same to be utilized at relatively low temperatures, below 900° F. and even below 800° F. in those instances where higher temperatures would be undesirable such as in the treatment of titanium, titanium alloys, and steel superalloys. This ability avoids aging of the material and various other disadvantageous phenomena such as hydrogen pickup, pitting, oxidation and the like as explained hereinabove.

Following the immersion, the metal is withdrawn from the alkali bath, preferably washed in water to remove any of the bath clinging to its surfaces, and pickled in a conventional manner in a dilute acidic material such as sulfuric acid, hydrochloric acid which may be in the form of sodium chloride added to the sulfuric acid, nitric acid, hydrofluoric acid and the like, alone or in admixtures, maintained at elevated temperatures, for example, in excess of about 100° F. to provide a clean bright surface. The pickling treatments may vary substantially in accordance with well known techniques.

The bath of this invention maintains its efficiency over extended periods, small quantities of additional material being added from time to time to replace losses occurring from dragout of the workpieces and their carriers, these intermittent additions maintaining both the volume and equilibrium of the bath.

Having now described the instant inventive concept in more general terms, the following specific examples will serve to illustrate the same although, it is to be understood that these examples are not to be interpreted as limiting.

Example 1

A 2600 pound charge of a material having the preferred formulation set forth above was added to a salt pot and heated to a temperature of approximately 900° F. Sec-

tions of glass-coated, scaled tubing 20 inches long by 3½ inches diameter having nonuniform vitreous bonded and fused coatings on their surfaces as much as ¼ inch thick in places resulting from a Sejournet-type extrusion process, were immersed in the bath for periods of times ranging from 30 seconds to several hours. The treated tubes were then withdrawn from the bath, quenched in water and pickled in a dilute acidic material in a conventional manner. Substantially all of the scale and glass were removed in most instances in a single immersion. In extremely difficult cases, a single reimmersion functioned to completely clean the surfaces, the final product having a bright, unmarred finish. Sludge was readily removed during the processing.

It was found that similar workpieces treated with prior art compositions required six to eight immersions before the surfaces were rendered substantially clean.

Example 2

The procedure of Example 1 was repeated immersing titanium workpieces having scaled surfaces formed by high temperature annealing processes in excess of 1200° C. and as high as 1450° C. The bath temperature was maintained between 800° F. and 900° F. The resulting products were completely descaled with no hydrogen pickup. Even reducing the temperature to from 700° to 800° F. resulted in excellent descaling while the bath viscosity remained sufficiently low to permit satisfactory desludging.

Similar titanium samples processed utilizing prior art materials required temperatures in excess of 900° F. to produce satisfactory descaling with the material picking up hydrogen resulting in detrimental effects from the standpoint of the physical characteristics of the titanium metal in subsequent operations.

Example 3

A procedure similar to Example 2 was utilized to descale particularly difficult alloys of titanium such as the following:

Type 481 containing 8 percent manganese;

Type 461 containing 5 percent aluminum and 2.5 percent tin;

Type 464 containing 6 percent aluminum and 4 percent vanadium; and

Type 120 VCA containing 13 percent vanadium, 11 percent chromium and 3 percent aluminum.

Completely satisfactory descaling of the above materials was realized at temperatures below 900° F. and even below 800° F.

Subjection of these same materials to prior art descaling techniques resulted in age hardening and other undesirable effects.

Example 4

Utilizing a procedure similar to Example 2, various samples of steel superalloys conditioned by heat treating and hot rolling thereby forming oxide coatings, were descaled, such as the following:

Multimelt (M)—chromium 18–22 percent, nickel 18–22 percent, molybdenum 2.75–3.75 percent, tungsten 2–3 percent, cobalt 18–22 percent, columbium .75–1.5 percent, the rest essentially iron;

Hastelloy X—chromium 20–23 percent, nickel 46 percent, molybdenum 8–10 percent, tungsten .2–1 percent, cobalt .5–2.5 percent, iron 17–20 percent;

Hastelloy B—molybdenum 26–30 percent, iron 4–6 percent, the rest essentially nickel;

Hastelloy C—chromium 13–17 percent, molybdenum 16–18 percent, tungsten 3.7–5.3 percent, iron 4.5–7 percent, the rest essentially nickel;

Haynes Alloy 25—chromium 19–21 percent, nickel 9–11 percent, tungsten 14–16 percent, iron 2 percent maximum, the rest essentially cobalt; and

René 41—chromium 11.5 percent, nickel 76 percent, silicon 4 percent, other elements 5 percent.

Complete descaling of these materials at temperatures below 900° F. and even below 800° F. has been effected with the salt remaining thin and fluid thereby facilitating desludging of the same.

Similar treatments of these and comparable superalloys with prior art compositions necessitated the use of temperatures in excess of 900° F. resulting in pitting, age hardening, galvanic attack and oxidation by the salt.

It will now be seen that there are herein provided compositions and methods for the cleaning of metals, specifically a large variety of normally difficult materials at relatively low temperatures, which satisfy all of the objectives of the instant application, and others, including many advantages of great practical utility and commercial importance.

Since many embodiments may be made of the instant inventive concept, and since many modifications may be made of the embodiments hereinbefore described, it is to be understood that all matter herein is to be interpreted merely as illustrative and not in a limiting sense. Accordingly what is claimed is:

1. A composition for the cleaning of metals consisting essentially of a fused, substantially anhydrous, mixture of from 9–15 weight percent sodium nitrate, from 5–15 weight percent sodium chloride, from 8–20 weight percent potassium hydroxide and from 50–78 weight percent sodium hydroxide, the weight ratio of potassium hydroxide to sodium hydroxide being at least 0.1 and not substantially in excess of 0.4.

2. A composition in accordance with claim 1 wherein said mixture consists essentially of 12 weight percent sodium nitrate, 10 weight percent sodium chloride, 15 weight percent potassium hydroxide and 63 weight percent sodium hydroxide.

3. A method for cleaning stainless steel and titanium base metals comprising immersing the metal to be treated in a molten bath consisting essentially of a mixture of from 9–15 weight percent sodium nitrate, from 5–15 weight percent sodium chloride, from 8–20 weight percent potassium hydroxide and from 50–78 weight percent sodium hydroxide, the weight ratio of potassium hydroxide to sodium hydroxide being at least 0.1 and not substantially in excess of 0.4, for at least 30 seconds, maintaining said bath at an elevated temperature above its melting point during the immersion, and removing the metal from said bath.

4. A method in accordance with claim 3 wherein said mixture consists essentially of 12 weight percent sodium nitrate, 10 weight percent sodium chloride, 15 weight percent potassium hydroxide and 63 weight percent sodium hydroxide.

5. A method in accordance with claim 3 further including the steps of washing the metal removed from said bath in water, and subjecting the same to a pickling treatment in a dilute acid solution.

6. A method of removing scale and glass from a stainless steel product manufactured by a high temperature process utilizing glass as a lubricating material comprising immersing the stainless steel product in a molten bath consisting essentially of from 9–15 weight percent sodium nitrate, from 5–15 weight percent sodium chloride, from 8–20 weight percent potassium hydroxide and from 50–78 weight percent sodium hydroxide, the weight ratio of potassium hydroxide to sodium hydroxide being at least 0.1 and not substantially in excess of 0.4 for at least 30 seconds, maintaining said bath at a temperature above its melting point during the immersion, and removing the stainless steel product from the bath.

7. A method in accordance with claim 6 wherein said mixture consists essentially of 12 weight percent sodium nitrate, 10 weight percent sodium chloride, 15 weight percent potassium hydroxide and 63 weight percent sodium hydroxide.

8. A method in accordance with claim 6 further including the steps of washing the stainless steel product

7

in water, and subjecting the same to a pickling treatment in a dilute acid solution.

9. A method of descaling a metal selected from the group consisting of titanium and alloys containing a predominant portion of titanium comprising immersing the metal to be treated in a molten bath consisting essentially of a mixture of from 9-15 weight percent sodium nitrate, from 5-15 weight percent sodium chloride, from 8-20 weight percent potassium hydroxide and from 50-78 weight percent sodium hydroxide, the weight ratio of potassium hydroxide to sodium hydroxide being at least 0.1 and not substantially in excess of 0.4 for at least 30 seconds, maintaining said bath at a temperature above its melting point and below about 900° F. during the immersion, and removing the metal from said bath.

10. A method in accordance with claim 9 wherein said mixture consists essentially of 12 weight percent sodium nitrate, 10 weight percent sodium chloride, 15 weight percent potassium hydroxide and 63 weight percent sodium hydroxide.

11. A method in accordance with claim 9 wherein said temperature is maintained at from 700°-800° F.

12. A method of descaling a wrought heat-resisting steel alloy comprising immersing the alloy to be treated in a molten bath consisting essentially of a mixture of from 9-15 weight percent sodium nitrate, from 5-15 weight percent sodium chloride, from 8-20 weight percent po-

8

tassium hydroxide and from 50-78 weight percent sodium hydroxide, the weight ratio of potassium hydroxide to sodium hydroxide being at least 0.1 and not substantially in excess of 0.4 for at least 30 seconds, maintaining said bath at a temperature above its melting point and below about 900° F. during the immersion, and removing the alloy from said bath.

13. A method in accordance with claim 12 wherein said mixture consists essentially of 12 weight percent sodium nitrate, 10 weight percent sodium chloride, 15 weight percent potassium hydroxide and 63 weight percent sodium hydroxide.

14. A method in accordance with claim 12 wherein said temperature is maintained at from 700°-800° F.

References Cited by the Examiner

UNITED STATES PATENTS

2,655,481	10/1953	Clingan	252-156 XR
2,931,778	4/1960	Ilenda et al.	252-156
3,030,239	4/1962	Mekjean et al.	252-156 XR

FOREIGN PATENTS

490,861	2/1953	Canada.
---------	--------	---------

25 JULIUS GREENWALD, *Primary Examiner*.

J. T. FEDIGAN, *Assistant Examiner*.