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ELECTROLYTIC FERROUS METAL CLEANING

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This invention relates to the art of cleaning work pieces of metal particularly to remove oxides and scales upon such metal. The greatest utility is in the treatment of ferrous metals typically iron of various carbon contents and which may contain typical alloying ingredients. More particularly this invention relates to treating such metals electrolytically to clean the surface thereof, and to a fused salt bath and chemical composition of such bath for this treatment.

In my prior Patent 2,468,006, issued April 19, 1949, I have described a bath composition comprising predominantly, caustic soda, containing minor quantities of sodium chloride and minor quantities of sodium aluminate. Small quantities of alkali metal fluoride may further be added to such bath, particularly where the metal to be cleaned contains sand inclusions. In operation of such bath electrolytically, with the work piece mounted as a cathode, the passage of electric current reduces the caustic soda to sodium metal. The sodium aluminate present in such bath provides oxygen which reacts with the sodium metal forming sodium monoxide which in turn decomposes and dissolves the scale or other oxides upon the metal being cleaned. The reduced aluminate in such baths reacts with further quantities of caustic soda to become regenerated as sodium aluminate and thereby is not used up in the operation. Thus small quantities of sodium aluminate suffice to operate over long periods of time. The sodium chloride in such bath serves to adjust the viscosity or fluidity of the bath composition at high temperatures in its molten state. The fluoride, when present, reacts with minor sand inclusions when such are present to aid in the dissolution thereof from the metal surface being cleaned. Only trace quantities of silica enter the bath, and then only when sand is present by cleaning of sand castings.

I have now found that an alkali metal fluosilicate such as sodium fluosilicate, will function in a fused caustic soda bath not only to remove sand inclusions from metal castings when such are present by the electrolytic effect to decompose the sodium fluosilicate to its components sodium silicate and sodium fluoride, but is also effective during electrolysis to supply oxygen to oxidize free sodium metal as formed at the cathode to sodium monoxide. This composition is thereby effective for cleaning of the scale or other oxide coating of the work being cleaned by electrolysis of the metal mounted in such fused metal bath composition as a cathode. During the electrolysis, the sodium monoxide is believed to remove the ferric or other metal oxide scale which in turn is dissolved by the caustic soda to form sodium ferrite ($Na_2Fe_2O_4$). The sodium fluoride operates directly upon any sand inclusions to dissolve them in the bath. However, upon termination of the cleaning and passage of current the sodium fluoride in the bath again reacts with the sodium silicate to form the sodium fluosilicate, as a stable form of the salt. Accordingly, it is also possible to substitute for the fluosilicate equivalent quantities of alkali metal silicate and alkali metal fluoride which react to generate the fluosilicate.

While the caustic-fluosilicate cleaning bath of the present invention operates in a manner analagous to the caustic soda aluminate, there are certain advantages over the caustic-aluminate bath which needs further to contain fluoride. The fluosilicate used as such, is of considerable advantage because of the economy. However, a greater advantage is in its effect to stabilize the bath to a desired fluidity, and also ready maintenance thereof over long periods of time in presence of impurities which accumulate in the bath with continued use.

The manner of operation of a caustic soda-fluosilicate bath is analogous to a caustic soda and aluminate bath in view of the activity of the fluosilicate during electrolysis to remove scale and accordingly, that fluosilicate containing bath will operate without aluminate. However, there are outstanding metal cleaning advantages in the aluminate of itself, as shown in my prior patent. Hence, it is oftentimes desirable to use both the fluosilicate and the aluminate in a combination for enhanced control over the fluidity of the bath over substantial periods of use, enhanced removal of sand inclusions in the metal and enhanced regeneration of aluminate in the bath as catalyst.

The fluosilicate for one or more of these purposes may be used in a wider range of proportions than would be used for the aluminate alone. Thus the alkali metal fluosilicate will be effective for its purposes in quantities ranging from about 0.5% to about 7% by weight of the bath composition to effect cleaning of the metal and control of fluidity. It is preferred however, to use the fluosilicate in quantities ranging from 4 to 6% by weight of the bath. The quantity of sodium aluminate when present, will be its usual catalytically small quantity range from 0.5 to 3%, and most commonly about 1%. Substantial control of the viscosity or fluidity of the bath is also and often more economically available by further additions of sodium chloride, and the quantity used will range from about 0 to 15%, most usually about 4 to 6%.

Thus, according to the present invention, a bath composition will comprise from 79 to 99.5 percent by weight of alkali metal hydroxide typically caustic soda, 0.5 to 7 percent by weight of alkali metal fluosilicate, 0 to 15 percent by weight of sodium chloride and 0 to 3 percent by weight of sodium aluminate. Thus, it will be noted, that the aluminate may be omitted, and the sodium chloride, usually used for its effect upon viscosity may also be omitted, with viscosity control being supplied by the fluosilicate. Moreover, in this formulation, the alkali metal fluosilicate may be substituted by equivalent quantities of alkali metal fluoride and alkali metal silicate each substantially stoichiometrically proportioned to the other to form alkali metal fluosilicate upon fusion in the presence of the caustic soda. The reaction of the fluosilicate in the bath to form sodium silicate and sodium fluoride during electrolysis, is illustrated by the following equation:

$$Na_2SiF_6+6NaOH \rightleftarrows 6NaF+Na_2SiO_3+3H_2O$$

In accordance with this equation sodium hydroxide of the bath reacts with the fluosilicate to form sodium silicate and sodium fluoride. Since the caustic soda is present in the bath in great excess, the bath, even after reacting according to the above equation, will still predominantly contain caustic soda. Thus, by starting with a major proportion of alkali caustic, and a substantial, but minor proportion, of alkali fluosilicate, the reaction provides sufficient alkali silicate and alkali fluoride in the bath to effect cleaning by electrolysis and the major proportion of the bath still remains as that part of the alkali caustic which is not chemically reacted with the

fluosilicate. Thus, the bath in a molten form and during electrolysis comprises in major part of caustic soda and minor parts of sodium silicate and alkali fluoride which reacts with the metal being cleaned during electrolysis to produce the cleaning action described above.

In a typical electrolytic cleaning by this invention the work piece to be cleaned, such as a ferrous metal casting containing sand inclusions as well as metal oxide scale, is first made part of the cathode, dipped to the fused bath containing both alkali and fluosilicate, subjected to 1000 amp. of current for each 4000 lbs. of bath substance and electrolyzed for about 15 minutes at a voltage drop of 6 to 2½ volts, at a temperature of about 850° F. Thereafter the current is reversed to make the work piece an anode for 15 minutes, and the current is finally reversed again to be cathodic for 10 minutes. The operation may be repeated and the electrolysis may be applied for longer periods before reversal as desired. Upon removal from the bath and washing free of molten salt, the metal is clean.

The following examples illustrate bath compositions within the scope of this invention:

Example I.—95 percent by weight of caustic soda, 5 percent by weight of sodium fluosilicate.

Example II.—85 percent by weight of sodium hydroxide, 7 percent of sodium fluosilicate and 8 percent by weight of sodium chloride.

Example III.—88.9 percent by weight of sodium hydroxide, 2 percent by weight of sodium silicate, 4.1 percent by weight of sodium fluoride and 5 percent by weight of sodium chloride.

Example IV.—90 percent by weight of sodium hydroxide, 5 percent by weight of sodium chloride and 5 percent by weight of sodium fluosilicate.

Example V.—89 percent by weight of caustic soda, 5 percent by weight of sodium chloride, 5 percent by weight of sodium fluosilicate and 1 percent by weight of sodium aluminate.

The molten salt bath, when ready for metal cleaning, may be operated at a temperature between 700 and 1000° F. However, the best operating temperature is believed to be between 800 and 850° F.

It can be seen that the chemical composition of the bath may be arrived at by first mixing the various chemicals as they are desired to appear in the molten bath in the dry state and then melting these chemicals, or in the alternative, the same bath can be obtained by mixing compounds which react to form the chemical composition desired in the bath.

I claim:

1. A process for electrolytic cleaning of ferrous metal which comprises immersing the metal in a dry solid molten salt bath comprising 75 to 99.5% by weight of alkali metal hydroxide and the remainder comprising a substantial proportion totalling at least 0.5% by weight of compounds comprising alkali metal silicate and alkali metal fluoride, said fluoride and silicate being each present in quantity sufficient to form at least 0.5 weight percent of alkali metal fluosilicate and cleaning the metal by passing current through said metal as an electrode while immersed in said bath.

2. A process for electrolytic cleaning of ferrous metal which comprises immersing the metal in a dry solid molten salt bath comprising 75 to 99.5% by weight of alkali metal hydroxide, and the remainder comprising a substantial proportion at least 0.5% by weight of an alkali metal fluosilicate, and cleaning the metal by passing current through said metal as an electrode immersed in said bath.

3. A process for electrolytic cleaning of ferrous metal which comprises immersing the metal in a dry solid molten salt bath comprising 75 to 99.5% by weight of alkali metal hydroxide, about 0.5 to 7% by weight of sodium fluosilicate, about 0 to 3% by weight of sodium aluminate and up to 15 parts by weight of sodium chloride, and cleaning the metal by passing current through said metal as an electrode while immersed in said bath.

4. A dry solid metal cleaning molten salt bath composition comprising a mixture of 75 to 99.5% by weight of alkali metal hydroxide, and the remainder comprising a substantial proportion at least about 0.5% by weight of alkali metal fluosilicate.

5. A dry solid metal cleaning molten salt bath composition comprising about 0.5 to 7% by weight of alkali metal fluosilicate, up to about 15% by weight of sodium chloride and the remainder caustic alkali.

6. A dry solid metal cleaning molten salt bath composition comprising a mixture of sodium fluoride and sodium silicate, said fluoride and silicate being each present in quantities sufficient to form at least 0.5 weight percent of alkali metal fluosilicate the total quantity of said mixture ranging from about 0.5 to 7% by weight, and the remainder comprising caustic alkali.

7. A dry solid metal cleaning molten salt bath composition, comprising about 0.5 to 7% by weight of sodium fluosilicate, and from 75 to 99.5% by weight of sodium hydroxide.

8. A dry solid metal cleaning molten salt bath composition, comprising a mixture of about 0.5 to 7% by weight of sodium fluosilicate, up to about 15% by weight of sodium chloride and the remainder caustic soda.

9. A dry solid metal cleaning molten salt bath composition, comprising about 90% by weight of sodium hydroxide, about 5% by weight of sodium chloride and about 5% by weight of sodium fluosilicate.

10. A dry solid metal cleaning molten salt bath composition, comprising about 0.5 to 7% by weight of sodium fluosilicate, up to about 15% by weight of sodium chloride, up to about 3% by weight of sodium aluminate and the remainder caustic soda.

11. A dry solid metal cleaning molten salt bath composition comprising a mixture of alkali metal fluoride and alkali metal silicate, said fluoride and silicate being each present in quantity sufficient to form at least 0.5 weight percent of alkali metal fluosilicate, the total quantity of said mixture ranging from about 0.5 to 7% by weight, up to about 3% by weight of sodium aluminate and the remainder comprising caustic alkali.

12. A dry solid metal cleaning molten salt bath composition comprising a mixture of about 89% by weight of caustic soda, about 5% by weight of sodium chloride, about 5% by weight of sodium fluosilicate and about 1% by weight of sodium aluminate.

References Cited in the file of this patent

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