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PROCESSES FOR REMOVAL OF OXIDES
FROM THE SURFACE OF METALS

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1

Our invention relates to a process for removal of dense, firmly adherent oxide formed on the surface of metals, through exposure to air, under high pressures, at elevated temperatures, by immersion of the metal in a fused anhydrous bath of caustic alkali containing an oxidizing agent, to convert the oxide to a form in which it is more reactive with acids, and then subjecting the modified oxide to the action of a dilute acid, as described and claimed in U. S. Patent No. 2,395,694, now re-issued as Patent No. Re. 22,887.

The process of the patents is stated therein to be useful for removal of surface oxides from iron, nickel and cobalt and their alloys with each other and with chromium, manganese, molybdenum, tungsten, vanadium and copper. The caustic alkalies suitable for the process are stated to include sodium and potassium hydroxide, and the oxidizing agents to include the alkali metal and alkaline earth chlorates, nitrates, chromates, manganates and permanganates.

In the above described process the efficiency of the fused bath is a function of its oxidizing capacity. With continued use of the bath its oxidizing capacity diminishes. It must therefore be restored in order that the bath be kept at high efficiency. Heretofore, the only method of doing so has been by addition of a further quantity of oxidizing agent.

The present invention has for its object to regenerate the oxidizing agent in situ, thus decreasing the consumption of oxidizing agent and increasing the capacity of a given equipment, in some cases with an actual improvement in the cleaning of the metal.

The oxidizing agents disclosed in the patents referred to may be divided into two groups as follows: (a) The chlorates, which in giving up their available oxygen are reduced to chlorides, which cannot be regenerated, so that substantial addition of oxidizing agent from time to time is necessary, in order that the bath may be constantly maintained at a high efficiency; and (b) Those, such as nitrates, manganates, permanganates, chromates, etc., which after reduction to a lower state of oxidation can be reoxidized to their former state. The oxidizing agents of group (b) which have become reduced are slowly reoxidized by the oxygen of the air when the bath is not in use. However, during the use of the bath at high output, the atmospheric reoxidation is too slow to keep pace with the reduction and the efficiency of the bath therefore falls off.

We have now found that the regeneration of

2

the oxidizing agents of group (b) can be accelerated by supplying elemental oxygen to the bath, as by bubbling air therethrough, either intermittently or while the bath is in use. The quantity of air may be quite small, e. g. 0.1 cubic foot per minute per ton of material in the bath. Contrary to expectation, this does not greatly increase the carbonate content of the bath.

We have also found that the regeneration of the oxidizing agent by exposure to the atmosphere is likewise accelerated by addition to the bath of a minor proportion, based on the oxidizing agent, of an oxygen carrier, i. e., a compound of a metal having a higher oxidation potential than that of the reduced oxidizing agent, hence capable of giving up oxygen thereto, and susceptible of atmospheric oxidation from a lower to a higher state of oxidation. This compound may be an oxide or a salt metal such as manganese, chromium, vanadium or molybdenum; or it may be a compound in which the metal occurs in the acid radical.

We have likewise found that if air is bubbled through the bath containing such an oxygen carrier the regeneration is still further accelerated and the capacity and effectiveness of the bath are thereby very notably increased.

Example I

For regeneration of the bath of caustic soda containing 4.07 per cent of sodium nitrite by oxidation of the nitrite to nitrate through contact with the atmosphere an exposure of 90 hours at 500° C. has been found necessary. If, however, air is bubbled through the bath, the time required for regeneration is decreased to 45 hours. If 0.5 per cent MnO_2 is added to the bath the time required for regeneration of the nitrate by exposure to the atmosphere at 500° C. is decreased to 11 hours; but if air is bubbled through the bath to which MnO_2 has been added, the time necessary for regeneration of the bath is further decreased to two hours.

Example I shows the manganese is highly effective as a carrier of oxygen to sodium nitrite, for the purpose of our process.

Example II

We have similarly found that regeneration of a bath of caustic soda containing 4.25 per cent sodium chromite, by oxidation of the chromite to 5 per cent chromate by exposure to the atmosphere at 500° C., requires 100 hours. This time is decreased to 80 hours if to the bath is added 0.5 per cent MnO_2 . The bath may be regenerated

in twenty hours by blowing air therethrough in the absence of manganese or in 5 hours by air blowing in presence of the manganese.

Example II shows that manganese is also effective as a carrier of oxygen to sodium chromite.

Example III

The following table affords an approximate comparison of the relative efficiency of various oxygen carriers as compared with MnO_2 , for accelerating regeneration of 4.07 per cent NaNO_2 to 5 per cent NaNO_3 at 500°C. , without air blowing.

Percent and Kind of Oxygen Carrier	Time of Regeneration, hours
None.....	90
0.5 MnO_2	11
0.5 MnSO_4	20
0.5 MnO_3	20
0.5 V_2O_5	20
2.0 CrO_3	20
5.7 Fe_2O_4	40

The above table shows that manganese is by far the most efficient oxygen carrier for our purpose and that MnO_2 is superior to MnSO_4 , probably because MnO_2 in fused caustic soda becomes sodium manganite, which oxidizes to sodium manganate and permanganate. This table further shows that while vanadium and molybdenum are likewise effective, chromium, which is always present in baths used for treating chrome steels, is poor, and iron, which is always present in baths used for treating ferrous metals is negligible, as an oxygen carrier.

It should be noted that the proportion of 0.5 per cent of oxygen carrier, given in the above table, which is calculated as the oxide, is not the minimum proportion necessary to yield a useful result, which depends on the particular oxygen carrier used and also upon whether it is assisted by air blowing. We believe the practical minimum to be 0.25 per cent without air blowing and 0.1 per cent if air blowing is used.

We are aware that it has been proposed in U. S. Patent 2,271,375, to add 0.5 to 10 per cent manganese dioxide or copper sulphate to a fused bath of caustic alkali containing an alkali metal nitrate, phosphate or carbonate, for the purpose of increasing the fluidity thereof; but this patent does not disclose that the nitrate becomes reduced to nitrite during use of the bath, that this slowly oxidizes back to nitrate through contact with the atmosphere; that such reoxidation is accelerated by presence of manganese or that the reoxidation is still further greatly accelerated by air blowing in presence of manganese.

It will be noted that among the oxidizing agents listed above as suitable for the process of the patents are the chromates and permanganates, which are also listed as oxygen carriers suitable for our present purpose. However, Example III shows that these are not all equally effective. The oxygen carrier should be in minor proportion with respect to the oxidizing agent, and preferably in the proportion of 0.5 to 1.0 per cent. The oxidizing agent and oxygen carrier may in fact be interchangeable, the latter being merely a minor addition of a different oxidizing agent. The present invention therefore contemplates, in the carrying out of the process of the patents referred to: (a) bubbling oxygen, as such or as air, through the bath of fused caustic alkali containing an oxidizing agent susceptible of oxidation from a lower to a higher state of

oxidation and an oxygen carrier capable of giving up oxygen to the reduced oxidizing agent and susceptible of oxidation from a lower to a higher state of oxidation, whether normally present or not, and (b) adding to such a bath such an oxygen carrier, not normally present in the bath, or in proportion greater than normally present, and contacting the bath with oxygen, either by exposure to the atmosphere or by bubbling the air therethrough.

Any suitable method and means may be used for introducing the air into the molten bath to be regenerated, as for example, bubbling the air below the surface of the bath through an iron pipe, preferably in such a way as to cause circulation of the bath.

In the process of the patents referred to, the oxidizing agent is preferably in minor proportion, e. g. 1 to 20 per cent, and preferably 5 to 10 per cent; however, we have found that the present process is particularly useful when the fused bath contains a relatively high proportion of oxidizing agent, e. g. 50 per cent or more, for the reason that baths containing such large proportions of oxidizing agents regenerate by surface exposure to air more reluctantly than when the oxidizing agent is present in minor proportion.

We claim as our invention:

1. In the removal of dense firmly adherent oxide from the surface of metals including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing an oxidizing agent stable therewith under the conditions of the process and susceptible of regeneration by oxidation from a lower to a higher state of oxidation, and a minor proportion, based on the oxidizing agent, of a material susceptible of oxidation to a state of oxidation in which it is capable of giving up oxygen to the reduced oxidizing agent, the method of accelerating the regeneration of the oxidizing agent, which comprises bubbling oxygen through the bath.

2. In the removal of dense firmly adherent oxide from the surface of metals including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing an oxidizing agent of the group consisting of the alkali metal and alkaline earth nitrates and chromates, and a minor proportion, based on the oxidizing agent, of an oxygen carrier of the group consisting of the alkali metal and alkaline earth compounds of manganese, vanadium, and molybdenum, the method of accelerating the regeneration of the oxidizing agent which comprises bubbling oxygen through the bath.

3. In the removal of dense, firmly adherent oxide from the surface of metals of the group consisting of iron, nickel and cobalt and other alloys with each other and with chromium, molybdenum, tungsten, vanadium and copper, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing not less than 1 per cent of sodium nitrate and 0.1 to 1.0 per cent of a compound of manganese stable with the bath, under the conditions of the process, calculated as manganese dioxide, the method of accelerating the regeneration of the oxidizing agent which comprises bubbling oxygen through the bath.

4. In the removal of dense firmly adherent oxide from the surface of metals, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic

5

alkali containing an oxidizing agent stable therewith under the conditions of the process and susceptible of regeneration by oxidation from a lower to a higher state of oxidation, the method of accelerating the regeneration of the oxidizing agent which comprises adding to the bath a minor proportion, based on the oxidizing agent, of a material susceptible of oxidation to a state of oxidation in which it is capable of giving up oxygen to the reduced oxidizing agent, and contacting the bath with air below the surface thereof to supply oxygen to the bath in excess over the normal exposure of the bath surface to the atmosphere.

5. In the removal of dense firmly adherent oxide from the surface of metals of the group consisting of iron, nickel, and cobalt and their alloys with each other and with chromium, manganese, molybdenum, tungsten, vanadium, and copper, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing an oxidizing agent of the group consisting of the alkali metal and alkaline earth nitrates, chromates, manganates and permanganates, the method of accelerating the regeneration of the oxidizing agent which comprises adding to the bath a minor proportion, based on the oxidizing agent, of a compound of a metal other than those undergoing treatment and in the oxidizing agent, susceptible of oxidation from a lower to a higher state of oxidation and in the latter state capable of giving up oxygen to the reduced oxidizing agent, and contacting the bath with air below the surface thereof to supply oxygen to the bath in excess over the normal exposure of the bath surface to the atmosphere.

6. In the removal of dense firmly adherent oxide from the surface of metals of the group consisting of iron, nickel, cobalt, and their alloys with each other and with chromium, manganese, molybdenum, tungsten, vanadium and copper, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali, containing an oxidizing agent of the group consisting of the alkali metal and alkaline earth nitrates, chromates, manganates and permanganates, the method of accelerating the regeneration of the oxidizing agent which comprises adding to the bath a material susceptible of oxidation to a state in which it is capable of giving up oxygen to the reduced oxidizing agent, in proportion minor with respect to the oxidizing agent, but substantially greater than normally present in the bath, and contacting the bath with air below the surface thereof to supply oxygen to the bath in excess over the normal exposure of the bath surface to the atmosphere.

7. In the removal of dense firmly adherent oxide from the surface of metals of the group consisting of iron, nickel, and cobalt and their alloys with each other and with chromium, molybdenum, tungsten, vanadium and copper, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing an oxidizing agent of the group consisting of the alkali metal and alkaline earth nitrates and chromates, the method of accelerating the regeneration of the oxidizing agent which comprises adding to the bath a minor proportion, based on the oxidizing agent, of an oxygen carrier of the group consisting of a compound of manganese stable with the bath under the conditions of the process, and con-

6

tacting the bath with air below the surface thereof to supply oxygen to the bath in excess over the normal exposure of the bath surface to the atmosphere.

8. In the removal of dense firmly adherent oxide from the surface of metals of the group consisting of iron, nickel, and cobalt and their alloys with each other and with chromium, molybdenum, tungsten, vanadium and copper, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali containing not less than 1 per cent of a reduced oxidizing agent of the group consisting of the alkali metal and alkaline earth nitrates and chromates, the method of accelerating the regeneration of the oxidizing agent which comprises adding to the bath 0.25 to 1.0 per cent of a compound of manganese stable with the bath under the conditions of the process, calculated as manganese dioxide, and contacting the bath with air below the surface thereof to supply oxygen to the bath in excess over the normal exposure of the bath surface to the atmosphere.

9. In the removal of dense firmly adherent oxide from the surface of metals, including the step of subjecting the oxide to the action of a fused substantially anhydrous bath of caustic alkali exposed to atmospheric oxygen and containing an oxidizing agent stable with the bath under the conditions of the process and susceptible of regeneration by oxidation from a lower to a higher state of oxidation, the method of accelerating the regeneration of the oxidizing agent which comprises maintaining in the bath a minor proportion, based on the oxidizing agent, of an oxygen carrier susceptible of oxidation to a state of oxidation in which it is capable of giving up oxygen to the reduced oxidizing agent at a rate effecting regeneration corresponding to an increase from approximately four percent NaNO_2 to approximately five percent NaNO_3 at a temperature of 500 degrees centigrade in not more than 20 hours, said carrier being selected from the group consisting of MnO_2 , MnSO_4 , MoO_3 , V_2O_5 , CrO_3 , and mixtures thereof.

10. The method of claim 9 wherein the oxidizing agent is present in minor proportion and wherein the oxygen carrier is present in the bath in about 0.25 to 1.0 percent by weight based on the oxidizing agent.

11. The method of claim 9 wherein the oxygen carrier is MnO_2 .

12. The method of claim 9 wherein the oxygen carrier is MnSO_4 .

13. The method of claim 9 wherein the oxygen carrier is MoO_3 .

14. The method of claim 9 wherein the oxygen carrier is V_2O_5 .

15. The method of claim 9 wherein the oxygen carrier is CrO_3 .

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