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RUSTPROOF MATERIAL AND PROCESS

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This invention comprises as a rustproofing material for iron and steel articles an artificial mineralogical analogue of magnetite which affords a corrosion protective surface of pleasing color and attractive appearance and the herein described electrochemical process of producing various artificial magnetite analogues.

It has long been common practice to apply magnetite (Fe_3O_4) by electrodeposit wherein the articles are used as anodes in an electrolytic bath of relatively high temperature thereby producing a black adherent coating which affords a considerable degree of protection against atmospheric corrosion. Such methods are not only expensive, but may alter the physical characteristics of the metal being treated, and the developed coating of magnetite contains impurities in exposed pores which afford points of corrosion attack and have necessitated the addition of an oil or lacquer treatment to render such coating impervious.

The present invention is predicated upon the discovery that mineralogical analogues of magnetite may be artificially produced, as herein-after described, and which when deposited upon exposed surfaces of articles to be rustproofed affords a very much greater degree of protection against corrosion by atmospheric agencies and chemical vapors than ordinary magnetite as heretofore used.

There occurs in nature a cupro-magnetite having the chemical formula CuFe_2O_4 and mineralogical formula $\text{CuO} \cdot \text{Fe}_2\text{O}_3$ and chrome-magnetite having chemical formula Cr_2FeO_4 and mineralogical formula $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$. It is said that a French scientist, Henri Moisson, succeeded by thermal methods in laboratory experimental production of a number of analogues of magnetite by substituting monoxides of several different metals for FeO in the mineralogical formula, but such magnetite analogues heretofore never have been artificially produced by electrochemical methods as herein described, and never have been commercially produced by any means nor the production thereof usably controlled.

The object of the invention is to produce upon iron and steel articles a protective surface finish which is impervious and strongly resistant to corrosion or rust, and which affords a pleasing color and attractive appearance.

A further and highly important object of the invention is the production of mineralogical analogues of magnetite by electrochemical process.

A further object of the invention is the control

of production and deposit of mineralogical analogues of magnetite.

A further object of the invention is the homogeneous combination of a magnetite analogue with an iron or steel article as a surface finish thereon.

A further object of the invention is to provide an impervious protective surface finish of great durability.

A further object of the invention is the use of mineralogical analogues of magnetite as a rustproofing and corrosion resistant material.

A further but none the less important object of the invention is to provide a practical commercially operable method of artificial production of various magnetite analogues.

With the above primary and other incidental objects in view as will more fully appear in the specification, the invention consists in the use of various mineralogical analogues of magnetite as rustproofing and corrosion resistant materials, and in the herein described process of artificial production of various magnetite analogues and their surface deposit upon iron and steel articles.

The present rustproofing material and its production includes the formation by electrochemical action on iron and steel surfaces of a double oxide of iron and some other metal, for example, copper, lead, tin, chromium, zinc, manganese, or nickel, thereby effecting an artificial analogue of magnetite (Fe_3O_4) wherein monoxides of either of the aforementioned metals are substituted for FeO. Thus in producing copper magnetite (CuFe_2O_4) CuO replaces FeO.

The process may be carried out in different ways, preferably however as the simultaneous deposit of the two metals in a single solution. The steps of the preferred method comprise use of a solution of caustic soda or of potash, having a concentration of approximately twenty to twenty-five percent by weight. Electrolysis between iron electrodes is effected therein at room temperature until the specific gravity of the solution has been increased about five percent at which time the bath assumes a deep violet color. If caustic soda has been originally employed the solution then comprises a mixture of sodium ferrite, ferric hydroxide, and sodium hydroxide. If potassium is used, the mixture will contain correspondingly potassium compounds.

An anode of the desired nonferrous material, (copper, chromium, lead, tin, zinc, manganese, nickel) is suspended in the solution and the iron or steel article to be treated is suspended therein

as the cathode. Upon circulation of current as in electroplating methods, at room temperature of approximately twenty to twenty-five degrees centigrade and with a current of approximately three and a half amperes per square decimeter, a tightly adherent impervious coating of high corrosive resistance and pleasing appearance forms upon the article (cathode) which chemical analysis shows to be an oxide film of both iron and the particular metal employed as the anode. The particular voltage requirement has not been found to be critical. It may vary according to working conditions as found necessary to maintain the requisite current density. The voltage ordinarily employed has varied from four to ten volts, best results being obtained with from six to ten volts. Experience has shown that the more exacting factors are first, the current density, that is, the total amount of current used proportionate to the surface area being coated in square decimeters, and second, the concentration of the solution. If the current density is materially increased, as for example fifty percent above that of 3.5 amps./dm.² mentioned, the deposit becomes coarse, granular and but loosely adherent. If the current density is materially reduced, the rate of deposit becomes too slow for practical commercial operation.

It is also found that above and below the range of solution concentration of 20-25% sodium hydroxide, the results rapidly become unsatisfactory.

It is not necessary that the scientific principle be explained nor even that it shall be known so long as the process or mode of operation which produces the result is disclosed, hence any statements of theory or principle contained herein are explanation only and not with intent to limit the character, scope or application of the invention. The exact reactions induced in the present instance are not positively known. There apparently occurs at the cathode a reduction of sodium or potassium ferrate from the solution and a simultaneous deposit of cupric oxide or black oxide of copper, chromium oxide or analogous oxides of such other metals which may be used as the anode material which apparently combine into a composite film of cupro-magnetite, chromite, or other analog of magnetite, tightly adherent to the article employed as the cathode.

In the case of artificial cupro-magnetite thus produced, it has been definitely ascertained that the copper is present as an oxide.

The resulting coating is not a mere smudge, but is sufficiently hard, deep and adherent to resist a reasonable amount of abrasion and polishing action and is of a grayish black color which becomes a brilliant black when lightly wiped with an oiled cloth.

The cathodic deposit of an oxide is believed to result from production of colloid hydroxides which are electro-positive colloids by the electrolytic corrosion of the anodes, and which migrate under suitable potential gradient to the cathode where they are reduced by nascent hydrogen to the oxide state. Just why these oxides show such marked affinity for the surface molecules of an iron body possessing negative polarity as to tenaciously attach themselves to the surface of even a smooth polished article so as to produce not a mere smudge, but a continuous tightly adherent corrosion resistant coating of appreciable depth, is yet not definitely known. The steps as described do produce such result which is amply sufficient for the present dis-

closure. When a copper anode is employed the copper ions travelling through the bath become a part of the molecular structure of the surface coating of the iron or steel cathode article. Likewise when chromium or ferro-chromium is employed, analysis shows the presence of chromium in such coating.

In lieu of such composite deposition of ferrous and nonferrous metals and codevelopment of such oxides the deposits may be separately electrochemically effected and subsequently unified by heat treatment.

Copper magnetite possesses the particular advantage over ordinary magnetite of being self healing. In event of rupture of its film in the presence of a corrosive agent capable of abstracting copper ions these will immediately deposit upon the bare iron in accordance with the well known electromotive series and will thereby seal against corrosion at such exposed spot.

The artificial chrome-magnetite in addition to the advantage of insolubility of chromite possesses a beautiful blue black color which enhances the appearance and increases the saleability of tools and other articles to which the finish may be applied.

Extensive corrosion tests show that the complex oxide finish herein described is much more resistant to corrosion than ordinary magnetite. Tests as to solubility, hardness, specific gravity, and refractive indices, particularly upon those specimens which have been heat treated show that the artificial magnetite analogues forming the subject matter hereof approach quite closely to the natural minerals which they simulate.

Since it is not necessary nor essential that an inventor shall state or even know the theory or principle upon which his invention is dependent, and in view of the generally unsettled state of scientific opinion regarding the mechanism of electrochemical reactions in such complex electrolytes, no explanation of such action is here attempted. It has been found, however, that working within the limits above mentioned and in the manner described, which have been stated for illustrative purposes only, and with no intent to unduly limit the scope or application of the invention, and employing an anode of nonferrous metal, there is effected by electrochemical action upon a cathodic article of iron or steel an oxide coating containing iron in combination with the particular metal used as the anode. Such magnetite analogue appears to be formed in the surface material of the article of which it becomes a homogeneous component and does not add appreciably to the weight thereof and is inseparable therefrom.

At present copper magnetite, tin magnetite and chromium magnetite have been found most efficient and desirable for commercial purposes, but it is to be understood that the invention is not limited thereto, but includes other mineralogical analogues of magnetite of which lead, zinc, manganese and nickel have been mentioned as examples. Likewise while the simultaneous deposit of the dissimilar metals in a single solution is preferred, their separate deposit and subsequent unification by heat treatment into a composite coating of a magnetite analogue of such metals is also within the contemplated scope of this invention.

The deposit resulting for the described process occurs very rapidly in its initial stages and is gradually retarded as the surfaces are covered until after a short period of time, ordinarily ten

to fifteen minutes under the temperature conditions, concentration of solution and amperage mentioned the action substantially ceases, affording, however, a very dense surface stratum of appreciable depth.

Having thus described my invention, I claim:

1. A metallic article including a double oxide surface coating of electrochemically deposited mineralogical analogue of magnetite comprising a double oxide of iron and a metal selected from a group of non-ferrous metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead.

2. An article of iron or steel including a rust-proof coating comprising a cathodic composite covering of an oxide of iron chemically combined with an oxide of a non-ferrous metal selected from a group of non-ferrous metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead.

3. A metallic article including a double oxide coating of rustproof material comprising a cathodic composite coating of an oxide of iron combined in intimate mixture with an oxide of a metal selected from a group of at least two of the metals specified.

4. An electrochemically deposited artificial mineralogical analogue of magnetite comprising an oxide of iron chemically combined with an oxide of copper.

5. A metallic article and a surface covering therefor of electrochemically deposited artificial mineralogical analogue of magnetite comprising an oxide of iron chemically combined with an oxide of chromium.

6. A metallic article and a surface covering therefor of electrochemically deposited artificial mineralogical analogue of magnetite comprising an oxide of iron chemically combined with an oxide of a metal selected from a group of at least two of the metals specified.

7. The herein described method of rustproofing iron or steel articles including the steps of providing an alkali bath of approximately twenty to twenty-five per cent concentration adding iron in solution to the bath, suspending therein as a cathode an iron or steel article to be treated, and an anode of a metal selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead and circulating electric current therebetween of approximately three and a half amperes per square decimeter of surface to be coated whereby there is deposited upon the cathode article a magnetite analogue of the anode metal.

8. The herein described method of effecting electrochemical deposit of a magnetite analogue including preparing a ferric hydroxide alkali electrolytic solution of approximately twenty to twenty-five per cent concentration, and subjecting thereto a ferrous cathode and an anode element selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead, and circulating an electric current therethrough having a density of approximately three and a half amperes per square decimeter whereby there is effected upon the cathode element a deposit of a magnetite analogue of the anode metal.

9. The herein described method consisting of providing a caustic alkali solution, electrolytically introducing iron in solution therein, suspending therein a ferrous cathode and a copper anode, circulating electric current of approximately three and a half amperes per square decimeter of

cathodic surface through the solution between the anode and cathode whereby a copper magnetite deposit will be produced upon the cathode.

10. The herein described method consisting of providing a caustic alkali solution inducing electrolysis between iron electrodes suspended in the solution, suspending therein a ferrous cathode and a chromium anode, circulating electric current of approximately three and a half amperes per square decimeter of cathode surface through the solution between the anode and cathode whereby a chromium magnetite deposit will be produced upon the cathode.

11. The herein described method of providing a corrosion resistant coating including utilizing an iron containing article to be coated as a cathode in a caustic alkali electroplating bath, utilizing therein an anode selected from a group of metals consisting of copper, chromium, zinc, tin, manganese, nickel and lead, and circulating therethrough an electric current of ample density to effect simultaneous electrochemical deposits of an oxide of iron and an oxide of the selected metal, the steps and procedure being such as to unify the deposits into a composite magnetite analogue.

12. The herein described method of providing a corrosion resistant coating including electrochemically depositing upon a cathodic article simultaneously deposits of an oxide of iron and an oxide of copper and thereby forming a composite coating of copper magnetite.

13. The herein described method of providing a corrosion resistant coating including simultaneously electrochemically depositing upon a cathodic article containing iron deposits of an oxide of iron and an oxide of chromium in the form of a composite coating of chromium magnetite.

14. A metallic article and a rustproofing coating therefor comprising an artificial analogue of magnetite.

15. A metallic article and a rustproofing coating therefor comprising a unified combination of oxides of iron and of a metal selected from a group consisting of copper, chromium, tin, zinc, manganese, nickel and lead.

16. A metallic article and a rust proof coating therefor comprising an electrochemical cathodic deposit of analogue of magnetite.

17. A metallic article and a rustproofing coating therefor comprising an electrodeposited double oxide of dissimilar metals including that of iron and a metal selected from a group consisting of copper, chromium, tin, zinc, manganese, nickel and lead.

18. The herein described method of coating ferrous articles consisting in employing such article as a cathode in an alkali hydroxide electrolytic bath of approximately twenty to twenty-five per cent concentration wherein the anode is of a metal selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead and maintaining therein a current density of substantially three and a half amperes per square decimeter of cathodic surface whereby there is deposited upon the cathodic surface a magnetite analogue of the anodic metal.

19. The herein described method of forming a double oxide coating upon a ferrous article including the steps of utilizing the ferrous article to be coated as the cathode in a caustic soda solution having a concentration of approximately twenty to twenty-five per cent by weight and employing therein a copper anode, and circulat-

ing electric current between said elements through the bath at a current density of approximately three and a half amperes per square decimeter to effect on the ferrous article simultaneous cathodic deposits of oxide of iron and oxide of copper.

20. The herein described method of forming a double oxide coating upon a ferrous article including temporarily utilizing the ferrous article to be coated as a cathode element in an alkali electrolytic bath, simultaneously employing therein an anode element containing copper and passing electric current between the elements through the electrolytic bath at a current density of approximately three and a half amperes per square decimeter of surface to be coated, thereby effecting upon the surface of the article a cathodic deposit of cupro-magnetite.

21. The herein described method of forming a double oxide coating upon a ferrous article including temporarily utilizing the ferrous article to be coated as a cathode element in an alkali electrolytic bath, simultaneously employing therein an anode element containing chromium and passing electric current between the elements through the electrolytic bath at a current density of approximately three and a half amperes per square decimeter of surface to be coated, thereby effecting upon the surface of the article a cathodic deposit of chromite.

22. The herein described method of surface coating ferrous articles including the steps of submitting the surface to be coated to cathodic oxidation in the presence of an alkali electrolyte containing iron wherein is utilized an anode element of a metal selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel and lead and circulating electric current between said elements of approximately three and a half amperes per square decimeter of surface to be coated thereby effecting upon the articles a cathodic deposit of a double oxide of iron and the anodic metal.

23. The herein described method of producing an analogue of magnetite including charging an alkali electrolytic bath of approximately twenty to twenty-five per cent concentration with iron entering into the solution, employing therein an anodic element selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel, and lead, and a cathodic element of

iron or steel, and circulating through such bath an electric current having a density of approximately three and a half amperes per square decimeter of cathodic surface whereby there will be deposited upon the cathodic element double oxide of iron and the selected anodic metal.

24. The herein described method of producing an analogue of magnetite including the step of utilizing an alkali electrolytic bath of approximately twenty to twenty-five per cent concentration, circulating an electric current through said bath between iron electrodes until the specific gravity of the solution is increased from two and a half to seven per cent, employing in said bath an anodic element selected from a group of metals consisting of copper, chromium, tin, zinc, manganese, nickel, and lead, and a cathodic element of iron or steel, and circulating through such bath an electric current having a density of approximately three and a half amperes per square decimeter of cathodic surface whereby there will be deposited upon the cathodic element double oxide of iron and the selected anodic metal.

25. The herein described method of producing copper magnetite including charging an alkali electrolytic bath of approximately twenty to twenty-five per cent concentration with iron by electrolysis between iron electrodes until the specific gravity of the bath has been increased two and a half to seven per cent, employing in said bath a copper anode and a ferrous cathode, and circulating therebetween an electric current having a density of approximately three and a half amperes per square decimeter of cathodic surface whereby there is deposited upon the cathodic element a double oxide of iron and copper.

26. The method of providing a corrosion resistant coating upon an article which consists in providing a caustic alkali solution, electrolytically introducing iron in solution therein, suspending a ferrous cathode and a non-ferrous anode of a metal selected from a group comprising copper, chromium, tin, zinc, manganese, nickel and lead, and passing an electrical current through the solution between the anode and cathode whereby there is obtained a composite coating upon the cathode of an oxide of iron chemically combined with an oxide of one of the non-ferrous metals used as the anode.

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