UNITED STATES PATENT OFFICE.

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PROCESS FOR RUST-PROOFING IRON AND STEEL.

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To all whom it may concern:

Be it known that I, WILLIAM H. ALLEN, a citizen of the United States, residing at Detroit, in the county of Wayne and State of Michigan, have invented a new and useful Process for Rust-Proofing Iron and Steel, of which the following is a specification.

This invention relates to the rendering rust-proof of iron and steel by changing the surfaces of these metals to basic phosphate salts of iron. Iron when placed in a solution of such acids as hydro-chloric, sulfuric or phosphoric, is attacked and dissolved, forming ferrous salts; in the case of the phosphoric acid, if the solution is weak, a more or less adherent coat of insoluble ferrous phosphate is formed, which, in the presence of an oxidizing agent becomes basic in character and black.

If a piece of iron is placed in a hot basic solution of ferric chlorid or ferric sulfate, there is formed a black basic salt adherent to the metal. When the iron is removed and placed in a hot solution of an alkali phosphate, such as tri-sodium phosphate or di-sodium phosphate, the adherent film becomes fairly permanent.

The governing of these reactions is quite difficult and impracticable. I have therefore invented the following process based upon the fact that the more acid phosphate salts of calcium, magnesium, barium or other alkali earth metals in solution react much less violently on iron than when free phosphoric acid is present.

As the acid radical (PO_4) is in union with the alkali earth metal (calcium for example), it will not readily form soluble iron phosphate, but readily forms the insoluble ferrous phosphate at the points of contact when iron is introduced. The soluble acid calcium phosphate ($2CaH_4(PO_4)_2$) (mono calcium phosphate) is converted into the insoluble acid calcium phosphate ($Ca_2H_2(PO_4)_2$) (dicalcium phosphate). If now, during the formation of the layer of ferrous phosphate, an oxidizing agent be present, some ferroso-ferric phosphates are formed and the surface of the iron becomes black. The reaction is probably as follows:

$$4CaH_4(PO_4)_2+8Fe+2O_2=2Ca_2H_2(PO_4)_2+Fe_3(PO_4)_2Fe_3O_4Fe_2(PO_4)_2+6H_2.$$

After removing from the solution, drying and oiling, the iron will resist corrosion by the atmosphere.

The oxidizing agents used are hydrated manganic oxid ($Mn_2O_3H_2O$) and air which is passed up through the solution in any desired manner. The proportions of the materials employed in preparing the bath are: mono-calcium phosphate 4 ounces, hydrated manganic oxid ½ ounce, water q. s. to make 1 gallon. These proportions may be modified to produce different thicknesses and densities of the protecting layers. The mono-calcium phosphate is also known as double super phosphate.

The solution is heated to nearly the boiling point and the objects of iron or steel are introduced. Air is forced up through the solution in fine streams, contact with the objects being avoided. When the desired color is obtained, the objects are removed, dried and oiled.

The hydrated manganic oxid may be prepared from either the commercial sulfate or chlorid of manganese, by dissolving it in water with an alkali such as caustic soda or slaked lime added to produce a faint alkalinity. The precipitated manganous hydrate, $Mn(OH)_2$, is separated and washed by decantation, and into the mud air is blown and the manganous hydrate is thereby rapidly converted into the hydrated manganic oxid

$$4Mn(OH)_2+2O=2Mn_2O_3H_2O+2H_2O.$$

It will be noted that practically no free phosphoric acid is present in this solution and that the affected surface of the article of iron or steel in the solution is not separated nor even has a tendency to separate from the main body of the article. As the acid radical is in union with the calcium, it will not form the soluble iron acid phosphate as in the case where free phosphoric acid is used.

I claim:—

1. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of an acid phosphate salt of the alkali earth metals in the presence of hydrated manganic oxid until a layer of suitable thickness of ferroso-ferric phosphate is formed.

2. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of an acid phosphate salt of the alkali earth metals in

the presence of hydrated manganic oxid until a layer of suitable thickness of ferroso-ferric phosphate is formed, a current of air being passed up through the solution.

3. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of mono-calcium phosphate in the presence of hydrated manganic oxid in water.

4. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of mono-calcium phosphate in the presence of hydrated manganic oxid in water while fine streams of air are being passed through the solution.

5. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of mono-calcium phosphate in the presence of hydrated manganic oxid in water practically free of free phosphoric acid.

6. The process of rendering the surfaces of iron or steel rust-proof which consists in immersing the same in a solution of an acid phosphate salt of an alkaline earth metal in the presence of a manganic oxid until a layer of non-rusting material of suitable thickness is formed.

In testimony whereof I have signed this specification.

WILLIAM H. ALLEN.