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COATING METAL

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This invention relates to coating metal; and it comprises a method of providing ferrous metal (iron and steel) or another oxidizable metal with a protective coating wherein the metal is dipped
5 in or wet with an alkaline aqueous solution containing barium and a permanganate; and it also comprises metal carrying a closely adherent protective dark colored film of oxid nature and containing barium, iron and manganese in various
10 states of oxidation; all as more fully hereinafter set forth and as claimed.

I have found that by dipping or otherwise wetting iron and steel in an aqueous bath containing barium hydroxid and a permanganate, the
15 metal is quickly covered with a dark colored protective coating layer useful in many relations. A solution containing 2 per cent barium hydroxid (as the octahydrate) and 1.5 per cent commercial permanganate is satisfactory. Formation of the
20 coating is accomplished in a minute or less. While work at the ordinary temperature is practicable, it is more rapid and generally satisfactory to operate in the temperature range between 60° and 100° C. The concentration of the components in the coating bath is not at all critical; the potassium permanganate concentration may
25 vary from 0.25 per cent to 3 per cent and that of the barium hydroxid octahydrate from 0.5 per cent to 5 per cent. Below these limits, the action of the solution is rather sluggish, while with solutions above the given limit, action is quite violent and adherence of the coating is not satisfactory.

The film formed is always dark, being dark green in color when present in very thin layers and green to purple in color when somewhat
35 thicker. The film is not injured and is indeed improved in some respects by heating. On heating for a minute or two at a temperature somewhat below red heat, the color of the coating is changed to a dull black.

While the stated solution made with potassium permanganate and crystallized barium hydrate is satisfactory, other ways of making the bath may be used. A solution of barium hydroxid and
45 barium permanganate is particularly satisfactory. Barium permanganate has the advantage of easy manufacture. Good results are obtained with a bath made up with sodium hydroxid, barium nitrate and potassium permanganate.

It is a well known fact that permanganate ion is rendered somewhat unstable by the addition of alkali, and long boiling of a concentrated solution of potassium permanganate and caustic potash results in some loss of oxygen and some formation of potassium manganate and also man-

ganese dioxid. Such solutions have, however, but slight tendency to coat iron and steel. Likewise, if a solution of potassium permanganate containing either strontium hydroxid or calcium hydroxid, but containing no barium ion, be heated to boiling and a sheet of clean iron introduced,
5 the tendency to coat iron is but little greater than if the solution were made up exclusively of alkali metal compounds. If, to such a solution, a small amount of any soluble barium salt be added, such as barium nitrate or barium acetate,
10 then the coating of the metal proceeds rapidly. Apparently, this tendency to coat iron and steel rises to a sharp maximum in the presence of hydroxyl ion, permanganate ion and barium ion; if one of these three components be absent, the
15 coating tendency is but slight or entirely absent. A solution in which the barium is replaced by lead basic acetate shows some tendency to coat iron but is quite inferior to the bath containing barium. It is not advantageous to use ammonia or an ammonium salt in such a bath because a violent action is set up between the ammonia and the permanganate, resulting in the oxidation of the ammonia to gaseous nitrogen, principally,
20 and the reduction of the permanganate to manganese dioxid. This reaction proceeds regardless of the presence or absence of metal.

The coating reaction takes place at the ordinary temperature but works more rapidly and
30 more satisfactorily at temperatures ranging between 60° C. and 100° C. It is believed that a reaction takes place between the iron or other metal and the permanganate which has been rendered unstable by the presence of barium ion and hydroxyl ion, resulting in the oxidation of the iron and the reduction of permanganates to manganates and to manganese dioxid. The property of coating metal under the conditions of the baths above described is peculiar to permanganate ion; it is not a property of manganate ion, since it was found that a solution of sodium manganate showed no tendency to coat iron either with a small amount of free caustic present or with a considerable amount of caustic alkali in
45 the bath.

The coating is believed to consist of a mixture of insoluble manganates, manganites and metallic oxids of iron, barium and manganese, alone or in combination.

As stated above, it is possible to have other
50 ions present in the bath in addition to the three whose presence is essential. For example, the addition of a soluble nitrate, such as barium nitrate or sodium nitrate, to the bath seems to re-

sult in a thinner but smoother and more uniform coating. Other substances which are compatible with the essential elements of the bath may be added for the purpose of improving or modifying the character of the coating.

In the preparation of metal for coating in the alkaline barium permanganate bath, the metal is ordinarily degreased and, if considerable rust or mill scale be present, is pickled to give a clean metallic surface. If the metal is a bright, cold rolled material, it may be degreased but need not be pickled as the bath coats clean unpickled metal as readily as though it had been pickled.

In a practical embodiment of the present process, clean ferrous metal is dipped into a bath containing two per cent of barium hydroxid octahydrate and 1.5 per cent potassium permanganate. The metal is held in the bath for one minute at a temperature of 90° C. It is then withdrawn, washed and dried. If the heat treatment is to be applied, it is heated at a temperature of 500° C. for 5 minutes. An addition to the bath of 3 per cent of sodium nitrate is beneficial in some cases. Other oxidizing agents having an effect similar to that of sodium nitrate may replace sodium nitrate.

As stated, the coating produced as described is useful in a number of ways. It may be oiled with linseed oil or another oil, such as Perilla oil, soya bean oil, etc., and the oil allowed to "dry", which it does with great rapidity. Manganese compounds are good drying agents and in this case, the proportion is large. And manganese compounds furnish oxygen; so that air drying is not essential. If a paint, lacquer or varnish containing a drying oil is applied over the coating and is then subjected to baking at an elevated temperature, the manganese compounds in the coating accelerate the hardening of the paint or varnish. The manganated coating forms an excellent substratum for oil varnishes, lacquers, enamels, etc. The coated metal may be redipped in one of the ordinary phosphate coating baths, giving a coating which is different from the ordinary phosphate coatings and is in many respects superior. The phosphated film is then a better rustproofing agent. For many uses, the manganated film may be simply oiled with a non-volatile wax or a heavy oil, or it may be treated with a bituminous or asphaltic composition, advantageously diluted or thinned with a volatile solvent. In some cases, the liquid may carry an oil soluble dye. An important new utility is preparing iron and steel for the application of vitreous enamels, compositions which are fused on the metal at a fairly high temperature. As is well known, it is difficult to prepare clean iron and steel so that a good bond is effected with this class of enamels. Sometimes, the metal is sand blasted, which is a good expedient but rather expensive.

The main utility of the new manganated film is, however, as a substratum for paints and lacquers. For this purpose, it may or may not be oiled or phosphated.

As stated, the coating bath may include nitrates. These are found to exercise an advantageous action in the coating process.

Non-ferrous oxidizable metals may be given a

manganated coating in the way described for iron and steel; the procedure and the final result being the same, save that iron is not now a component of the film, an oxid of the other metal (copper, tin, zinc, brass, lead, etc.) taking its place.

What I claim is:—

1. The process of producing a protective coating on an oxidizable metal of a class consisting of iron and steel, zinc, brass, copper, tin and lead which comprises treating the surface of the metal with a solution comprising a soluble permanganate, a soluble barium compound and a soluble hydroxid, washing the resulting coating free from mother liquor and drying it.

2. The process of producing a protective coating on an oxidizable metal of a class consisting of iron and steel, zinc, brass, copper, tin and lead which comprises treating the surface of the metal with a solution containing a soluble permanganate, a soluble barium salt, a soluble metal hydroxid and an oxidizing agent other than permanganate.

3. The process of claim 1 wherein the metal to be treated is ferrous metal.

4. The process of claim 2 wherein the second oxidizing agent is a soluble nitrate.

5. The process of claim 1 wherein the permanganate ion is present as an alkali metal permanganate.

6. The process of claim 1 wherein the soluble barium compound is barium hydroxid.

7. A solution for the production of protective coatings on oxidizable metals which comprises permanganate ion, barium ion and hydroxyl ion.

8. A solution for the production of protective coatings on oxidizable metal containing barium permanganate and barium hydroxid.

9. As a new material, an oxidizable metal of a class consisting of iron and steel, zinc, brass, copper, tin and lead bearing a coating produced by the action on the metal of a solution comprising permanganate iron, barium ion and hydroxyl ion.

10. Ferrous metal carrying a surface coating produced by the action upon the metal of a solution comprising permanganate iron, barium ion and hydroxyl ion.

11. Ferrous metal carrying a dark protective coating of oxid nature, containing iron, barium and manganese, and formed by action upon the metal of an alkaline solution containing barium permanganate, the manganese in the coating being in various stages of oxidation lower than the permanganate stage.

12. Ferrous metal carrying an adherent manganated coating formed upon the metal by a coating solution comprising permanganate ion, barium ion and hydroxyl ion and a finish coat of oil, paint, varnish lacquer or enamel bound to the metal by said manganate coating.

13. Ferrous metal carrying an adherent manganated coating formed upon the metal by a coating solution containing barium permanganate and barium hydroxid and a finish coat containing a drying oil baked upon and hardened by said manganate coating.

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