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PROCESS OF COATING METAL SURFACES

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This invention relates broadly to the treatment of metal articles for the preparation of the metal surfaces to resist rusting or corrosion and to receive surface coatings of various sorts and in some cases for the improvement of characteristics of the metal articles, and the present application is a continuation in part of my prior application Ser. No. 36,217, filed August 14, 1935, resulting in Patent 2,244,526, June 3, 1941.

The primary object of the invention is to provide a process of treating surfaces of iron, steel, ferrous alloys, copper and cuprous alloys to render them resistant to rusting, oxidation and corrosion and better adapted to receive and retain surface coatings such as paint, lacquer and non-vitreous enamels (either natural or synthetic resin or cellulosic): vitreous enamels and all manner of metal coatings whether deposited electrolytically or by hot dipping, rolling, tumbling or spraying processes.

Another object is to provide a process of imparting to metal articles a finish which does not interfere with electric or acetylene welding or brazing and which serves to diminish or inhibit electrolytic action between different metals.

Various other objects and the advantages of the invention may be ascertained from the following description.

In its broadest aspect, the invention comprises, firstly, subjecting the articles to be treated to the action of a molten coating agent comprising an alkali metal phosphate or mixture of alkali metal phosphates with the addition of one or more of the alkali metal nitrates, and, if desired, with the further addition of alkali metal carbonate. To any of these mixtures there may be added an oxygen carrying agent, a fluxing agent or a stabilizing agent; secondly, treating the articles with a neutralizing solution and thirdly and optionally treating the articles with a colouring, sealing and finishing solution. The articles may be washed with water as may be desired or necessary between the several treatments.

More particularly, the invention comprises the features and combinations of features herein disclosed together with all such modifications thereof and substitutions of equivalents therefor as are within the scope of the appended claims.

The invention is primarily intended to provide a durable and attractive surface finish on ferrous and cuprous and aluminous metallic articles, independently of any other surface coating and which finish is resistant to rusting, oxidation and corrosion of the metal and forms an improved foundation for other surface coatings.

The treatment is effected most conveniently by immersing the articles to be treated in baths of the various materials used but other means of effecting the treatment may be adopted. For convenience, in the description only the bath method will be referred to but it will be understood the invention is not thereby limited to the bath method. In carrying out the complete process the articles are immersed in three baths in succession, namely:

First: a molten cleaning, stripping and coating bath;

Second: a neutralizing bath;

Third: a sealing and/or colouring finishing bath.

The molten bath is composed essentially of an alkali metal phosphate or mixture of alkali metal phosphates in admixture with one or more of the alkali metal nitrates, and hydroxides, and if desired, alkali metal carbonate, with or without bath fluxing or stabilizing agents, or both. For treating iron, steel and ferrous alloys, it is preferred that the predominant constituent of the bath be a mixture of alkali metal phosphate, with one or more of the alkali metal nitrates and possibly alkali metal carbonate, and that the alkali metal hydroxides, if used at all, be present in minor proportion; but for treating copper, brass and bronze, it is preferred that alkali metal phosphate or mixtures thereof with alkali metal nitrate or nitrate and carbonate, and an alkali metal hydroxide or mixture of alkali metal hydroxides be present in about equal proportions. Thus, for treating iron, steel and ferrous alloys, 66% or more of the molten bath is preferably composed of mixtures of alkali metal phosphate with one or more of the alkali metal nitrates and carbonates and the remainder, being 34% or less, is composed of one or more of the alkali metal hydroxides. For treating copper and its alloys, the bath is composed preferably of about 50% of a mixture of alkali metal phosphate with one or more of the alkali metal nitrates and carbonates and about 50% of alkali metal hydroxide. The addition of a small proportion of manganese dioxide or crystalline copper sulphate as a flux improves the fluidity of the bath and thus reduces the loss through dragout on the articles treated. The manganese dioxide has oxidizing and also catalytic or accelerating action. The amount of either manganese dioxide or copper sulphate should be between 0.5% and 10% of the bath and preferably is about 1% or 2%. Copper sulphate appears also to have a stabilizing effect on the bath, especially at higher temperatures.

If it is desired to impart the most effective rust and corrosion retarding finish to the surface of the metal, the bath temperature should be between 500° and 900° F. and preferably between 700° and 900° F. The actual temperature used depends upon the composition of the bath, the metal treated and the duration of the treatment, which last depends upon the necessity, or otherwise, of first removing an existing coating. As the duration of treatment depends to some extent on the temperature, the nature of the articles immersed will have some influence. Thus, comparing a compact casting and a thin plate of equal surface areas, the casting will require somewhat longer immersion on account of heat loss from the bath to the casting.

The molten bath reacts with the metal to produce a very strongly adherent coating practically integral with the metal, which is an excellent retardant of rust and corrosion. This coating is so thin it does not cause any significant increase in the dimensions of the articles treated. Screws or bolts with very fine threads are not appreciably tighter in cooperating tapped holes after treatment than before treatment. Thin steel sheets treated as described may be bent back and forth at small radius curvature with no apparent detriment to the surface finish until about the time fracture of the metal occurs. The coating is, moreover, a better foundation for paint, lacquer, non-vitreous and vitreous enamels and metal plating such as zinc, tin, cadmium, copper, nickel, and the like (electrolytic, hot dip, tumbled or rolled) than the metal of the article itself and such surface coatings applied to articles treated according to this invention are more adherent than when applied to bare metal.

Articles to be treated in the molten bath are merely immersed therein and no agitation of the articles or of the bath is necessary. The material of the bath is very penetrating and goes into the most minute crevices. Metal plates closely packed together receive as good a finish on the contact surfaces as on exposed surfaces and do not show any traces of the contact such as would occur in electroplating or after dipping in paint or enamel. Small articles such as bolts, nuts, washers and the like may be treated in bulk in baskets.

After immersion in the molten bath, the articles are lifted out, drained for a few seconds and then washed with water either by immersion therein or by spraying. The washing should be more thorough if the molten bath contains a large percentage of sodium or potassium hydroxide than if it contains only a little or none at all.

The washed articles are next immersed in a neutralizing bath being a weak aqueous solution of hydrochloric, sulphuric, oxalic or other suitable acid or an aqueous solution of iron sulphate, maintained preferably at a temperature of about 160° F., but the temperature may be lower or higher, for example, from 100° to 200° F. A 1% to 2% solution of hydrochloric acid will serve while sulphuric or oxalic acids may be used up to 5%. The preferred bath is iron sulphate, about 4 ounces to each imperial gallon of water. This solution not only neutralizes any alkali adhering to the metal but darkens and improves the appearance of the finish imparted in the molten bath.

After treatment in the neutralizing bath, the articles may be discharged and used as they are or may be painted, enamelled or metal plated, but

it is preferred that they be transferred to a finishing bath, preferably after washing to remove any free acid from the surface thereof. This finishing bath is composed of iron sulphate, crystalline haematoxylin, water soluble nigrosine, tannic acid or other suitable sealing or colouring agent in solution in water. The bath is made up with any of the above ingredients present in proportion of approximately 4 ounces to 1 imperial gallon of water. Instead of crystalline haematoxylin, an equivalent amount of logwood chips or any of the other logwood preparations may be used. The amounts of reagents used may be either more or less than above stated. This bath is maintained preferably at a temperature of approximately 180° F., but the temperature may be lower or higher, for example between 100° and 200° F., and the articles are immersed therein for two to ten minutes and then removed and washed with water. The resulting finish is more resistant to rust and corrosion than that produced in the first bath and is a better base for paint, enamel and metal plating. The finish is of very good appearance, ranging from "gun metal" to dark blue or black. If given a coat of oil or clear lacquer, the appearance is similar to good black enamel. In addition to colouring the finish imparted in the first bath, the materials used enter the pores or intermolecular spaces of the finish and seal the same against entrance of rust or corrosion producing agents.

The neutralizing bath is very important if a paint, lacquer or enamel is to be applied subsequently as every trace of alkali must be removed to avoid the appearance of blemishes in the final coating.

The condition of the second and third baths should be tested from time to time as to acidity and alkalinity and adjusted as necessary by addition of acid or other ingredient to correct the condition.

Steel articles which have been tempered or case hardened may be treated according to this invention without affecting the temper or hardness. Also, the finish imparted does not interfere with electric or acetylene welding or brazing.

Specific examples of various molten bath formulae are given below but it will be understood the invention is not in any way limited to the materials or proportions of the examples.

FIRST BATH

Example I

	Parts
Trisodium phosphate.....	3
Potassium nitrate.....	2

Example II

Trisodium phosphate.....	3
Sodium hydroxide.....	2

Example III

Trisodium phosphate.....	4
Potassium nitrate.....	1
Sodium hydroxide.....	1

Example IV

Trisodium phosphate.....	4
Sodium carbonate.....	1
Sodium hydroxide.....	2

Example V

Trisodium phosphate.....	2
Potassium phosphate.....	2
Sodium hydroxide.....	4

Example VI

	Parts
Trisodium phosphate-----	2
Potassium phosphate-----	2
Sodium nitrate-----	2
Sodium hydroxide-----	2

Example VII

Trisodium phosphate-----	2
Potassium nitrate-----	3

Example VIII

Trisodium phosphate-----	2
Sodium hydroxide-----	3

Example IX

Trisodium phosphate-----	2
Sodium nitrate-----	3
Sodium hydroxide-----	1

Example X

Trisodium phosphate-----	2
Sodium carbonate-----	1
Sodium hydroxide-----	3

Example XI

Trisodium phosphate-----	2
Potassium nitrate-----	1
Potassium hydroxide-----	3

Example XII

Trisodium phosphate-----	50
Sodium hydroxide-----	50

In preparing any of the molten baths, it is essential to first melt the nitrate or hydroxide or mixture thereof and then add the phosphate gradually holding the bath temperature as low as possible until all the phosphate has been added and melted into the bath. To any of the foregoing mixtures there may be added, if desired, from 0.5% to 10% of manganese dioxide or crystalline copper sulphate as a fluxing and stabilizing agent, the preferred amount being 1% to 2%.

In any of the foregoing examples, the alkali metal compounds named may be replaced by the similar compound of the other alkali metal.

Instead of trisodium phosphate, there may be substituted any of the other sodium phosphates, but trisodium phosphate is preferred on account of its melting point and ready miscibility in the fused state with other alkali metal compounds and because of its activity in producing the desired coatings.

The surface finish imparted according to this invention, and especially that resulting from immersion in all three baths, is very durable and tenacious, so that metal sheets thus treated may be formed in dies without injuring the finish.

The finishing treatment, especially when temperatures between 600° and 900° F. are used, has an annealing effect which improves the strength of the metal. In certain cases where annealing is required between forming operations, the parts may be treated according to this invention between the forming operations and annealing thus effected simultaneously with surface finishing. It is possible also to heat the bath above 900° F., say to 1200° or even 1500° F., to heat treat articles for removal of internal stresses therefrom or for other purposes.

If no subsequent surface coating is to be applied, it is preferable to use iron sulphate in the second or neutralizing bath and the third bath may be omitted, but a better appearing

finish and one more resistant to rust and corrosion is obtained if the articles are treated in the third bath also. It is usually preferable to use iron sulphate in one only of the baths, that is, if it is used in the second bath one of the other agents is used in the third bath, but if the sulphate is to be used in the third bath, the second bath is preferably made with hydrochloric or other acid.

Having thus described my invention, what I claim is:

1. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate and alkali metal nitrate, the resulting mixture being in the molten state reactive with the metal treated to produce a coating thereon, and subjecting the articles to the action of the molten mass.

2. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate and alkali metal hydroxide, the resulting mixture being in the molten state reactive with the metal treated to produce a coating thereon, and subjecting the articles to the action of the molten mass.

3. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate, alkali metal nitrate and alkali metal hydroxide, the resulting mixture being in the molten state reactive with the metal treated to produce a coating thereon, and subjecting the articles to the action of the molten mass.

4. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate, alkali metal carbonate and alkali metal hydroxide, the resulting mixture being in the molten state reactive with the metal treated to produce a coating thereon, and subjecting the articles to the action of the molten mass.

5. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate, alkali metal nitrate and alkali metal carbonate, the resulting mixture being in the molten state reactive with the metal treated to produce a coating thereon, and subjecting the articles to the action of the molten mass.

6. A process according to claim 1 in which the mixture has added to it manganese dioxide.

7. A composition of matter for use as a molten bath in surface coating ferrous and cuprous articles comprising the product resulting from fusing together a mixture of alkali metal compounds including alkali metal phosphate and alkali metal nitrate.

8. A composition of matter for use as a molten bath in surface coating ferrous and cuprous articles comprising the product resulting from fusing together a mixture of alkali metal compounds including alkali metal phosphate and alkali metal hydroxide.

9. Ferrous and cuprous articles having on the surface and in the pores thereof a tenaciously adhering rust and corrosion resisting coating produced by subjecting the articles to the action of a molten mass resulting from fusing together

a mixture of alkali metal compounds including alkali metal phosphate and alkali metal nitrate.

10. Ferrous and cuprous articles having on the surface and in the pores thereof a tenaciously adhering rust and corrosion resisting coating produced by subjecting the articles to the action of a molten mass resulting from fusing together a mixture of alkali metal compounds including alkali metal phosphate and alkali metal hydroxide.

11. The process for producing a protective coating on ferrous, rust susceptible metallic surfaces which consists in subjecting such surfaces to a molten bath consisting of hydroxide and a phosphate.

12. The process for producing a protective coating on ferrous, rust susceptible metallic surfaces that consists in subjecting such surfaces to a molten bath consisting of sodium nitrate, sodium hydroxide, and a phosphate.

13. The process for producing a protective coating on ferrous, rust susceptible metallic surfaces which consists in subjecting such surfaces to a molten bath composed of chemicals including hydroxide and a phosphate.

14. The process for producing a protective coating on ferrous, rust susceptible metallic surfaces which consists in subjecting such surfaces to a molten bath consisting of hydroxide, an oxidizer and a phosphate.

15. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including alkali metal phosphate as the essential ingredient and manganese dioxide, the resulting mixture being in the molten state reactive with the metal treated to produce a strongly adherent coating thereon, and subjecting the articles to the action of the molten mass.

16. A process of coating articles of iron, copper, and alloys of each of them, which process comprises fusing together a mixture of alkali metal compounds including trisodium phosphate as the essential ingredient, the resulting mixture being in the molten state reactive with the metal treated to produce a strongly adherent coating thereon, and subjecting the articles to the action of the molten mass.

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