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PROCESS OF TREATING 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.

The primary object of the invention is to provide a process of treating surfaces of iron, steel, ferrous alloys, copper and cuprous alloys and aluminum and its 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, roling, tumbling or spraying processes.

Still 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 one or more of the alkali metal nitrates, phosphates, carbonates and hydroxides with or without the addition of one or more of;—an oxygen carrying agent, a fluxing agent, 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 one or more of the alkali metal nitrates, phosphates or carbonates with or without the addition of one or more of an alkali metal hydroxide and bath fluxing and/or stabilizing agents. For treating iron, steel and ferrous alloys, it is preferred that the predominant constituent of the bath be an alkali metal nitrate, phosphate or carbonate and that alkali metal hydroxides, if used at all, be present in minor proportion; but for treating copper, brass, bronze and aluminum, it is preferred that a nitrate (or phosphate or carbonate) and an hydroxide be present in about equal proportions. Thus, for treating iron, steel or ferrous alloys, the molten bath is preferably composed of 66% or more of sodium or potassium nitrate, phosphate or carbonate and 34% or less of sodium or potassium hydroxide, but if desired there may be less than 66% of nitrate, phosphate or carbonate and more than 34% of hydroxide. For treating copper and its alloys and aluminum, the bath is composed preferably of about 50% of sodium or potassium nitrate, phosphate or carbonate and about 50% of sodium or potassium 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 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.

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, enameled 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.

A beautiful black finish may be imparted to aluminum by dipping in the molten bath at a temperature between approximately 440° and 460° F. and preferably about 450° F. for one to two minutes and then letting the articles stand for thirty minutes to two hours before washing.

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
Sodium nitrate	5
Potassium nitrate	1

Example II

Sodium nitrate	parts	5
Potassium nitrate	do	5
Sodium hydroxide	per cent	1

Example III

	Parts
Trisodium phosphate	4
Sodium hydroxide	1
Potassium nitrate	1

Example IV

	Parts
Potassium carbonate	8
Sodium hydroxide	2

Example V

	Parts
Potassium nitrate	65
Sodium hydroxide	34

Example VI

	Parts
Sodium hydroxide	50
Potassium nitrate	50

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.

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.

Claims to the use of an alkali metal phosphate in a coating process, also claims to such a coating composition, and claims to the coated product are presented in my co-pending application for patent Serial No. 284,557, filed July 14, 1939.

Claims to the use of an alkali metal carbonate in a coating process, also claims to such a coating composition, and also claims to the resultant coated product are presented in my co-pending application Serial No. 284,558, filed July 14, 1939.

Claims to the use of an alkali metal hydroxide in a coating process, also claims to such a coating composition, and also claims to the resultant coated article are presented in my co-pending application for patent Serial No. 284,559, filed July 14, 1939.

Claims to a process of cleaning the surface of iron, copper, and alloys of each of them, with a molten mixture of certain of the alkali metal compounds, and claims to such a composition, are presented in my copending application for patent Serial No. 284,560, filed July 14, 1939.

Having thus described my invention what I claim is:

1. A process of coating articles of iron, copper, aluminum and alloys of each of them with a tenaciously adhering rust and corrosion resisting film capable of constituting a superior foundation for paint, lacquer, vitreous enamel and metal platings, which process comprises subjecting the articles to the simultaneous action of a molten alkali metal nitrate, a molten alkali metal hydroxide and manganese dioxide, constituting a bath in which the articles are immersed.

2. A process of coating articles of iron, copper, aluminum and alloys of each of them with a tenaciously adhering rust and corrosion resisting film capable of constituting a superior foundation for paint, lacquer, vitreous enamel and metal platings, which process comprises subjecting the articles to the action of a molten bath initially comprising manganese dioxide, potassium nitrate and an alkali metal hydroxide and subjecting the thus treated articles to the action of an aqueous solution including haematoxylin as a surface sealing and colouring agent.

3. A process of coating articles of iron, copper, aluminum and alloys of each of them with a tenaciously adhering rust and corrosion resisting film capable of constituting a superior foundation for paint, lacquer, vitreous enamel and metal platings, which process comprises subjecting the articles to the action of a molten mixture comprising potassium nitrate, sodium hydroxide and manganese dioxide and then subjecting the articles to an aqueous solution including haematoxylin as a surface sealing and colouring agent.

4. A composition of matter for use as a molten bath in surface coating ferrous, cuprous or aluminous articles, comprising potassium nitrate, sodium hydroxide and manganese dioxide.

5. Ferrous, cuprous and aluminous articles having on the surface and in the pores thereof a tenaciously adhering rust and corrosion resisting film produced by subjecting the articles to the action of a molten mixture comprising an alkali metal nitrate, an alkali metal hydroxide and manganese dioxide.

6. A process of coating articles of iron, copper, aluminum and alloys of each of them with a tenaciously adhering rust and corrosion resisting film capable of constituting a superior foundation for paint, lacquer, vitreous enamel and metal platings, which process comprises subjecting the articles to the action of a molten mixture of alkali metal compounds including an alkali metal nitrate, the said molten mixture being capable of reaction with the metal articles with production of a rust and corrosion resisting film coating on the surface of the articles, said mixture having added to it manganese dioxide and copper sulphate, and subsequently subjecting the film coated articles to the action of a colouring and sealing agent in aqueous medium capable of absorption into said surface film and finally washing the articles with water until unabsorbed colouring and sealing agent is removed.

7. A process of coating articles of iron, copper, aluminum and alloys of each of them, which comprises fusing together a mixture of alkali metal compounds including alkali metal nitrate as the essential ingredient together with alkali metal hydroxide and manganese dioxide, the resulting mass 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.

8. A process of coating articles of iron, copper, aluminum and alloys of each of them, which comprises fusing together a mixture of alkali metal compounds including potassium nitrate, sodium hydroxide and manganese dioxide, the resulting mass 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.

9. A composition of matter for use as a molten bath in surface coating ferrous, cuprous and aluminous articles comprising the product resulting from fusing together potassium nitrate, sodium hydroxide and manganese dioxide.

10. A composition of matter for use as a molten

bath in surface coating ferrous, cuprous and aluminous articles comprising the product resulting from fusing together alkali metal nitrate, alkali metal hydroxide and manganese dioxide.

11. Ferrous, cuprous and aluminous 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 including manganese dioxide, alkali metal nitrate and alkali metal hydroxide.

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