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PROCESS OF APPLYING BONDING COATING
TO METAL AND PRODUCT THEREOFLeo P. Curtin, Cranbury, N. J., assignor to
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corporation of DelawareNo Drawing. Application April 16, 1937,
Serial No. 137,377

8 Claims. (Cl. 148-6.5)

This invention or discovery relates to processes of applying bonding coatings to metals and products thereof; and it comprises a method of coating ferrous metal articles with films adapted to serve as a bonding layer for paints and varnishes and formed in part at the expense of the metal, in which a minor amount of copper is preliminarily deposited on the article as a subvisible layer, partly covering the surface and leaving it partly exposed so as to form a large number of minute galvanic couples and thereby activate the surface, and afterwards there is applied a bonding coat, for example, an oxy-sulfide or phosphate coating, adherence of the coating to the underlying metal being improved by the action of the copper deposit; and it further comprises a ferrous metal article carrying copper in minute localized spots over its surface and a bonding coat thereover; all as more fully hereinafter set forth and as claimed.

In preparing sheet iron and steel for painting, lacquering, etc., it is best practice to provide the metal with a coating of some sort which will serve to furnish a bond between the paint and the metal. The bonding coating sometimes is, and sometimes is not, a true protective coating (rust-proof coat) in and of itself. Its primary function is to adhere firmly to the metal on the one hand and to the paint on the other. Various bonding coatings are known. Phosphating treatments are widely used, adapted to yield phosphate coatings of low solubility; and in a co-pending application, Serial No. 137,376, filed April 16, 1937, I have disclosed and claimed provision on metals of an improved bonding coating comprising metallic oxides and sulfides, formed by action upon the metal of acid sulfites and similar salts. Most of the bonding baths attack the iron, and the coating they produce includes greater or less proportions of iron derived from the article itself.

The surface produced by the attack carries the coating and much depends on the evenness of attack; the coating should adhere to the metal with equal firmness at all points. With most of the regular coating baths, it is not difficult to get a uniform, permanent coating upon ordinary, clean iron surfaces; but with certain iron articles, difficulties are experienced, due to the character of the iron surface; chiefly to its lack of uniformity. This is often true, for example, in the case of sheet steel which has been subjected to drastic cold rolling. Such steel may have a bright silvery surface, which in some respects resembles passivated iron. It resists etch-

ing or attack by most chemical reagents, except ferric chloride and does not readily yield metal for forming a coating. Upon subjecting it to usual rust-proofing baths, the deposit formed may be spotty and irregular. On the other hand such metal is particularly ill-adapted to receive a paint coat directly, and provision of a bonding coat is a desideratum. Iron articles prepared in other ways besides drastic cold rolling may have similar inert surfaces. In general, highly burnished iron surfaces or portions thereof may resist the action of bonding baths.

According to the present invention I modify iron surfaces, prior to subjecting the articles to a bonding bath, in such manner that the bonding reagent will react with the surface uniformly and rapidly. In the best way known to me of achieving this result, I subject the iron surface, prior to coating it, to the action of a solution containing a compound of copper (or other metal below iron in the electromotive series) capable of depositing out on the iron by replacement. Copper sulfate is on the whole the most suitable reagent, while copper chloride, acid phosphate, acetate and nitrate work well. The conditions of treatment are adjusted so that a mere sub-visible deposit of copper is formed, and the metal deposits as a vast number of localized minute flecks or spots with intervening spaces of bare metal (iron). When an iron article so treated is immersed in a bonding bath, the bonding coat forms in a rapid and remarkably uniform and regular manner, whatever may be the state of the iron surface as regards activity. The copper deposit activates the iron, so to speak, probably by production of innumerable galvanic couples (copper-iron). Whatever the explanation, the improvements result as described.

The copper bath is advantageously maintained slightly on the acid side of neutrality; though useful results can be obtained with various alkaline copper solutions, for example, ammoniacal solutions of copper and also solutions of copper salts in caustic alkalis.

Referring to copper sulfate baths, the bath advantageously contains from 0.025 to 0.20 per cent of commercial copper sulfate pentahydrate. The acidity is maintained by supplying from 0.01 to 2 per cent of free sulfuric acid on the weight of the bath. Instead of sulfuric acid, sodium bisulphate may be used. A mixture of 4 parts finely divided bluestone (crude hydrated copper sulfate) with 96 parts powdered sodium bisulphate is a convenient composition for making up

a bath. 12.5 grams of this mixture dissolved in a liter of water makes a satisfactory bath.

The working temperatures are advantageously kept low, say from 16 to 25° C., and immersion of an iron article in the bath for 15 seconds is sufficient.

In operation, an iron article to be coated is degreased in known manner and then dipped in the bath for a short length of time. It is then removed and rinsed. To the naked eye there is no evidence that copper has been deposited on the metal; it looks much the same before and after the treatment. However, analysis discloses traces of copper and the ability of the metal to receive bonding coatings is greatly enhanced. The iron thus treated takes coatings of the phosphate, oxalate, oxide, oxide-sulfide or other types regularly and uniformly. And furthermore these coatings, especially the phosphate and oxide-sulfide coatings, have improved adherence and rust resistance especially when coated with lacquer films.

It is important to arrest the coppering operation prior to formation of any substantial or continuous film visible to the naked eye. This requires a short period of immersion and weak solutions. Higher temperatures than those mentioned can be used but if so, the dipping time should be shortened or the copper solution made more dilute.

In an example of a specific embodiment of the invention, the material to be treated was a batch of iron sheets cold-rolled under such conditions that they had a mirror-like silvery appearance over most of their surface and did not take on a good coating by being merely immersed in oxide-sulfide or in phosphate baths in the usual way. The sheets were degreased and rinsed in known ways and then dipped for 15 seconds in a cold solution containing 0.05 per cent blue vitriol and 0.50 per cent sulfuric acid. The sheets were then removed, rinsed and immersed in an oxide-sulfide coating bath made up according to the specification of my copending application Serial No. 137,376; such a bath containing 30 parts sodium bisulfite (NaHSO_3) and 90 parts zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) to each 880 parts of water, for example, with or without the inclusion of a fraction of a per cent of sulfuric acid of sodium bisulfate to increase its acidity. The resulting coating contains oxidized zinc, ferrous oxide, and sulfide; and it appears that zinc oxide and zinc sulfide are present as such in the coating. The sulfide content of the coating is substantial, although the metallic constituents are apparently present largely as oxides, and it is believed that the coating contains complex metallic oxy-sulfides. This oxide-sulfide coating adhered tightly to all parts of the sheets. The coated sheets were lacquered. The bond was excellent; the lac-

quered sheets standing up exceptionally well under the salt spray and other endurance tests.

Solutions of metals below iron in the electromotive series suitable for the preliminary treatment of the ferrous article, which can advantageously be used, are silver, lead and tin.

What I claim is:

1. A method of coating ferrous metal articles with films adapted to bond paints and varnishes thereto, comprising subjecting the article to treatment with an acidified solution of a metal below iron in the electromotive series for a length of time sufficient to cause traces of the metal to be deposited on the article in the form of localized minute specks with intervening spaces of bare iron but insufficient for the production of any continuous or thick metallic film, and subsequently subjecting the article to treatment in a bath adapted to produce a bonding coating thereon.

2. A method of coating ferrous metal articles with film adapted to bond paints and varnishes thereto, comprising subjecting the article to the action of an acidified copper solution for a length of time sufficient to produce a slight deposition of copper in the form of localized minute specks with intervening spaces of bare iron and insufficient to form a continuous metallic film, removing the article from contact with the copper solution and applying to it a bonding coating.

3. A method of coating ferrous metal articles with films adapted to bond paints and varnishes thereto, comprising cleaning the article, subjecting it to the action of an acid copper sulfate solution of 0.2 per cent concentration or less of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ for a length of time sufficient to produce a slight deposit of copper in the form of localized specks upon the surface of the article with intervening bare spots, rinsing the article and subsequently applying a bonding coating.

4. The method of claim 3 wherein the coppered metal is treated in an acid sulfite coating bath forming a metallic oxide-sulfide continuous adherent bonding coat.

5. The method of claim 1 wherein the bonding coating subsequently applied is an oxide-sulfide coating.

6. The method of claim 1 wherein the bonding coat subsequently applied contains metallic phosphates of low solubility.

7. A ferrous metal article on which is a discontinuous deposit of firmly adherent, minute localized particles of a metal below iron in the electromotive series, a superposed bonding coat and a siccative coat on top of the bonding coat.

8. A ferrous metal article carrying copper in minute localized spots over its surface, a bonding oxide-sulfide coating superposed on the coppered surface and a siccative coating on top of the bonding coating.

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