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METHOD OF SPOT-WELDING PHOSPHATED METAL ARTICLES

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The present invention relates to a method of preparing a spot-welded metal article. In a more particular sense, it relates to the preparation of a spot-welded, phosphated ferrous metal article by a method which is both convenient and economical.

The application of aqueous phosphating solutions in the metal finishing and fabricating art is both wide-spread and well-known. Such solutions provide means for forming an adherent, inorganic phosphate coating on a metal surface, which coating protects the metal substrate against corrosion and serves as an excellent base to receive topcoats of organic finishes such as paint, enamel, varnish, alkyd resins, etc.

Before the present discovery, the use of phosphating processes had been seriously curtailed, principally because metal surfaces which had been phosphated could not be "spot-welded" satisfactorily. Spot-welding is the term commonly applied in the welding industry to a method of welding together metal surfaces by passing a very high amperage electrical current through a small area of contact thereof, causing the metal to fuse in that area and, upon cooling, to form a strong joint or "spot-weld." Conventional commercial phosphate coatings appear to interfere with the passage of the welding current and result in poor welds and/or premature destruction of the electrodes by excessive arcing. Indeed, the unsuitability of phosphated metal surfaces for spot-welding has become so widely recognized that the instruction manuals of leading manufacturers of spot-welding equipment generally caution against the practice.

Any phosphating process adds to the cost of finishing a metal article and, in many instances, this added cost becomes prohibitive when a metal article, especially one made in a production line, must first be formed and spot-welded before it is phosphated. The formed and spot-welded article may be of such dimensions and shape that it cannot be phosphated conveniently over its entire surface by ordinary commercial phosphating procedures. Although it is possible to phasphate unformed steel, particularly rolls of steel strip stock, by high speed, low cost, dip-phosphating or spray-phosphating processes in a continuous manner, the spot-welding of such phosphated steel has been unsuccessful for the very reasons indicated earlier. Thus, a definite need has existed for a method of preparing a spot-welded, phosphated metal article from phosphated metal stock, particularly phosphated, light-gauge, steel strip stock.

It is, therefore, a principal object of the present invention to provide a method for preparing a spot-welded, phosphated metal article.

A further object is to provide a convenient and economical method for the preparation of a spot-welded, phosphated ferrous metal article.

A still further object is to prolong the useful life of spot-welding electrodes in the preparation of spot-welded, phosphated metal articles.

These and other objects are achieved by means of a method which comprises (A) phosphating a metal article with an aqueous phosphating solution containing as essential ingredients zinc ion, phosphate ion, nitrate ion, and a cation selected from the group consisting of lithium, berryllium, magnesium, calcium, strontium, cadmium, and barium to form thereon an integral phosphate coating, and then (B) spot-welding said phosphated metal article.

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The novel phosphating solutions essential for the purposes and practice of this invention are described in detail in co-pending U.S. application Ser. No. 373,449, filed August 10, 1953, by John A. Henricks, now Patent No. 3,090,709. It is intended that the entire disclosure of the said Henricks application be incorporated herein by reference. The acidic, aqueous phosphating solutions described therein preferably have a total acidity within the range from about 5 to about 100 points and contain as essential ingredients zinc ion, phosphate ion, nitrate ion, and a cation selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium. Such phosphating solutions provide a dense, adherent, micro-crystalline or amorphous phosphate coating which shows substantially no visible crystal structure at a magnification of 100 diameters. The "points" total acidity or total acid referred to above, represents the number of milliliters of 0.1 normal sodium hydroxide solution required to neutralize a 10 milliliter sample of the phosphating solution in the presence of phenolphthalein as an indicator. Generally a total acidity within the range from about 5 to about 100 points, preferably from about 5 to about 50 points, is required to obtain phosphating solutions which are capable of providing commercially satisfactory coating weights and speeds.

Of the various phosphating compositions disclosed in application Ser. No. 373,449, a particularly effective and useful sub-group for the purposes of the present invention includes those which have a total acidity within the range from about 5 to about 100 points and contain as essential ingredients from about 0.1 to about 1.0 percent of zinc ion; from about 0.25 to about 2.0 percent of phosphate ion; from about 0.25 to about 8.0 percent of nitrate ion; and from about 0.1 to about 4.0 percent of a cation selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium.

Best results from the standpoint of excellence of the phosphate coating and economy of ingredients are obtained when the phosphating step of the present invention is carried out by means of an aqueous phosphating solution having a total acidity within the range from about 5 to about 50 points and containing as essential ingredients from about 0.1 to about 0.6 percent of zinc ion; from about 0.3 to about 1.5 percent of phosphate ion; from about 0.5 to about 6.0 percent of nitrate ion, and from about 0.1 to about 1.5 percent of calcium ion. In certain instances, the additional presence of the ammonium ion is desirable.

In view of the extensive commercial development of the phosphating art and the many journal publications and patents describing the application of phosphating solutions, it is believed unnecessary to lengthen this specification unduly by a detailed recitation of the many ways in which the phosphating step may be accomplished. Suffice it to say that any of the commonly used phosphating techniques such as spraying, brushing, dipping, or roller-coating may be employed, and that the temperature of the aqueous phosphating solution may vary within wide limits, e.g., from room temperature to about 212° F. In general, best results are obtained when the aqueous phosphating solution is used at a temperature within the range from about 150° F. to about 210° F. If desired, however, the aqueous phosphating bath may be used at higher temperature, e.g., 225° F., 250° F., or even 300° F., by employing superatmospheric pressures.

In the ordinary practice of phosphating a metal surface, such surface is first cleaned by physical and/or chemical means to remove any grease, dirt, or oxides, and then it is phosphated in the manner described earlier.

The phosphating operation is usually carried out until the weight of the phosphate coating formed on the metal surface is at least about 25 milligrams per square foot of surface area and is preferably within the range from about 100 to about 1000 milligrams per square foot of surface area. The time required to form the phosphate coating will vary according to the temperature, the type of phosphating solution employed, the particular technique of applying the phosphating solution, and the coating weight desired. In most instances, however, the time required to produce a phosphate coating of the weight preferred for the purpose of the present invention will be within the range from about one-quarter minute to about 15 or 20 minutes. Under certain circumstances, however, such as the immersion of hot (300°–700° F.) steel in a phosphating solution, the steel is phosphated almost instantaneously.

Upon completion of the phosphating operation, the phosphated article is rinsed, optionally, with water and/or a dilute aqueous solution of chromic acid containing from about 0.01 to about 1.0 percent of chromic acid. The chromic acid rinse appears to "seal" the phosphate coating and improve its utility as a base for the later application of paint, lacquer, varnish, and the like.

Specific examples of phosphating solutions which yield phosphate coatings suitable for the purpose of the present invention are shown in Table I (values given are the percentages by weight of the several ions in the aqueous phosphating solution).

TABLE I

Phosphating solution

Ion	A	B	C	D	E	F	G
Zn	0.52	0.48	0.44	0.33	0.13	0.21	0.5
PO_4	1.29	1.22	1.1	0.83	0.41	0.45	1.3
Ca	0.27	0.85	0.78	0.18	0.1	0.12	0.5
NO_3	1.41	5.36	3.2	0.93	0.53	0.55	1.7
NH_4	0.14	0.13	0.12	------	------	------	------
Cl	0.22	------	------	------	------	------	------
ClO_3	------	------	------	------	------	0.05	0.17
Points total acid	30	30	30	20	10	11	25

The above phosphating solutions can be made conveniently by dissolving zinc dihydrogen phosphate in water to supply the required zinc phosphate ions, and then adding a nitrate of one or more metals of the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium. Finally the acidity of the solution (i.e., the points total acid) is adjusted by the addition of small amounts of phosphoric acid or nitric acid. Alternatively, the solutions can be made by dissolving zinc nitrate in water and then adding a phosphate of at least one metal of the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium. As indicated above, the acidity of the resulting solution may then be adjusted by the addition of small amounts of phosphoric acid or nitric acid.

The ions of the bath used in the practice of this invention may be derived from a variety of compounds and it appears to be of little consequence whether or not these ions come from different salts or acids. Regardless of the identity of the salts selected to provide the required ions, the resulting bath is effective to serve the purpose of this invention. It is necessary only that these salts or acids be used in amounts to provide the necessary concentration of the required characterizing ions. In addition to the characterizing ions present in the phosphating bath, certain supplementary ions such as chloride, bromide, ammonium, chlorate, perchlorate, nitrite, or perborate ions may also be present to control coating speed, increase the rust-inhibiting qualities of the coating, reduce sludging, etc.

The presence of the lithium, beryllium, magnesium, calcium, strontium, cadmium, or barium ion serves to suppress the formation of massive, hydrated crystalline coatings and yield instead the micro-crystalline or amorphous coating required for the purpose of the present invention. The nitrate ion serves as an oxidizing agent to depolarize the metal surface and increase the coating speed of the phosphating solution. Its presence is essential in the phosphating solutions employed for the purpose of the present invention.

By way of illustration, solution A in Table I was prepared by dissolving in sufficient water to make one liter of solution, 14.2 grams of $Zn(NO_3)_2 \cdot 6H_2O$, 7.8 grams of commercial 75 percent H_3PO_4, 4.2 grams of $ZnCl_2$, 8.7 grams of $NH_4H_2PO_4$, and 14.3 grams of

$$Ca(NO_3)_2 \cdot 3H_2O$$

Solution B in Table I was prepared by dissolving in sufficient water to make one liter of solution, 21.4 grams of $Zn(NO_3)_2 \cdot 6H_2O$, 7.2 grams of commercial 75 percent H_3PO_4, 8.4 grams of $NH_4H_2PO_4$, and 18.1 grams of $Ca(NO_3)_2 \cdot 3H_2O$.

After the metal article has been provided with a micro-crystalline phosphate coating, it may be post-treated as indicated earlier, by rinsing it with water and/or a dilute aqueous solution of chromic acid. In lieu of the chromic acid rinse, it is also feasible to use a dilute solution of calcium dichromate and/or zinc dichromate with or without a small amount of phosphoric acid. Although such post-treatments of the phosphated metal article are highly desirable, it should be emphasized that they are not prerequisites to satisfactory spot-welding. Their only function is to improve the corrosion-inhibiting properties of the phosphate coating.

The phosphated article is now fully prepared for spot-welding. This operation may be carried out by the use of procedures and equipment commonly employed for the purpose. No special precautions are necessary and adjustments with respect to welding current, welding time, and electrode pressure on work may be made in the manner known to those versed in the art of spot-welding.

It has been found that the tensile shear strength of a spot-welded phosphated metal article according to the present invention is fully equivalent to that of a conventional, spot-welded, uncoated metal article. Thus, the advantages of a metal article of this invention with respect to corrosion resistance and paint adhesion are achieved with no sacrifice of weld strength. Furthermore, tests indicate that the method of this invention substantially extends the life of spot-welding electrodes by minimizing arcing and "metal spitting."

The following examples are submitted to illustrate specific modes of carrying out the present invention. They are presented for purpose of illustration only and are not to be construed as limiting the scope of the appended claims.

EXAMPLE 1

A large number of clean, degreased, 4-inch x 12-inch panels of SAE 1020 20-gauge cold-rolled steel were spray-phosphated for 70 seconds at 160–165° F. with an aqueous phosphating solution containing 0.15 percent zinc ion, 0.54 percent phosphate ion, 1.40 percent nitrate ion, and 0.39 percent calcium ion, and having a total acidity of 12 points. Thereafter the panels were water-rinsed, sprayed for about 30 seconds at 70° F. with a 0.01 percent aqueous solution of chromic acid, water-rinsed again, and dried. The phosphate coating weight on the panels was found to be 190±10 milligrams per square foot.

Pairs of the phosphated panels were then abutted along their 12-inch dimension and spot-welded with a commercial spot-welding machine equipped with ⅝-inch Class II alloy electrodes having $\frac{7}{32}$-inch diameter flat faces. The force of the electrodes against the work was 360 pounds and the welding current was maintained at about 7500 amperes ±5 percent in accordance with American Welding Society Class B weld specifications.

Very satisfactory welds were obtained in $\frac{10}{60}$ of a second per spot and after 1448 spot-welds were made, the electrodes were still in good condition and did not require dressing.

According to well-recognized industry standards, uncoated steel panels should give satisfactory welds in $^{21}/_{60}$ of a second per spot and the attainment of 1000 welds without electrode dressing is considered to be excellent.

Thus, the welding process of this invention meets or exceeds industry specifications and offers, in addition, the known corrosion-inhibiting and paint-adhesion characteristics of a phosphated metal surface.

At periodic intervals during the experiment described in Example 1, 1-inch x 4-inch coupons were made from the phosphated steel panels. Pairs of these coupons were abutted along their 1-inch dimensions and each pair was given a single $^{10}/_{60}$ second spot-weld under the welding conditions followed in Example 1.

The spot-welded coupons were then subjected to the Tinnius-Olson Tensile Test to determine their tensile shear strength. Each coupon tested was identified by a "weld number" which indicated the specific number of the weld with respect to the set of electrodes used. The test results are shown in Table II.

TABLE II

Weld No.:	Tensile shear strength, pounds
1	1,120
112	1,100
252	1,180
493	1,140
494	1,160
534	1,200
616	1,160
1196	1,190
Average	1,155

The results given in Table II indicate that welds of consistent tensile shear strength are produced by the method of the present invention throughout the normal life (ca. 1000 welds) of an electrode. Furthermore, each individual result and the average result are well within the industry specification of 1230 pounds ±17 percent tensile shear strength for the specific welding conditions used. Thus, the welding method of this invention involves no sacrifice of either weld strength or weld repeatability.

What is claimed is:

1. A method of preparing a spot-welded, phosphated metal article which comprises (A) phosphating a metal article with an aqueous phosphating solution containing as essential ingredients zinc ion, phosphate ion, nitrate ion, and a cation selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium to form thereon an integral phosphate coating, and then (B) spot-welding said phosphated metal article.

2. A method according to claim 1 characterized further in that the metal article of (A) is a ferrous metal article.

3. A method according to claim 1 characterized further in that the aqueous phosphating solution of (A) has a total acidity within the range from about 5 to about 100 points.

4. A method according to claim 1 characterized further in that the aqueous phosphating solution of (A) additionally contains the ammonium ion.

5. A method of preparing a spot-welded, phosphated metal article which comprises (A) phosphating a metal article with an aqueous phosphating solution containing as essential ingredients zinc ion, phosphate ion, nitrate ion, and calcium cation, and then (B) spot-welding said phosphated metal article.

6. A method of preparing a spot-welded, phosphated ferrous metal article which comprises (A) phosphating a ferrous metal article with an aqueous phosphating solution having a total acidity within the range from about 5 to about 100 points and containing as essential ingredients from about 0.1 to about 1.0 percent of zinc ion; from about 0.25 to about 2.0 percent of phosphate ion; from about 0.25 to about 8.0 percent of nitrate ion; and from about 0.1 to about 4.0 percent of a cation selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium, to form thereon an integral phosphate coating of at least about 25 milligrams per square foot of surface area; and then (B) spot-welding said phosphated ferrous metal article.

7. A method of preparing a spot-welded, phosphated ferrous metal article which comprises (A) phosphating a ferrous metal article with an aqueous phosphating solution having a total acidity within the range of from about 5 to about 50 points and containing as essential ingredients from about 0.1 to about 0.6 percent of zinc ion; from about 0.3 to about 1.5 percent of phosphate ion; from about 0.5 to about 6.0 percent of nitrate ion; and from about 0.1 to about 1.5 percent of calcium ion to form thereon an integral phosphate coating of from about 100 to about 1000 milligrams per square foot of surface area; and then (B) spot-welding said phosphated ferrous metal article.

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