

UNITED STATES PATENT OFFICE

2,346,302

METHOD AND MATERIAL FOR COATING
METAL SURFACES

Noble E. Hays and George R. Hoover, Middle-
town, and Alva E. Taylor, West Middletown,
Ohio, assignors to The American Rolling Mill
Company, Middletown, Ohio, a corporation of
Ohio

No Drawing. Application August 2, 1940,
Serial No. 350,076

15 Claims. (Cl. 148—6)

This invention relates to the coating of zinc surfaces with a substantially insoluble coating of phosphates which renders said surfaces particularly advantageous for the reception and retention of paints, enamels and the like.

The difficulties encountered in coating zinc surfaces, such as on galvanized sheets, with paints, enamels, or other siccative coatings are well known. Difficulty is experienced in applying the coating and there is a tendency for it to become brittle and peel off in a comparatively short time.

Various surface treatments have been suggested to overcome this difficulty, the most successful of which is commonly known as Bonderizing. While this name is not limited to the treatment of zinc, the solution commonly called by this name which has proved most successful for zinc is one in which the zinc surface is treated in a solution containing phosphoric acid, phosphates, nitrates and a small amount of another metal which is commonly iron. A more detailed description of the chemical features of these processes is contained in other patents, as for example Nos. 1,869,121; 2,082,950; and 2,067,214.

While coatings produced by this treatment have proved very successful with respect to their superior ability to receive and hold paint, fabricators of galvanized sheets have experienced considerable difficulty in spot welding material which has been given this treatment. Owners of large and powerful spot welding machines found that they could not regularly make successful welds on this material in the cheap and rapid manner demanded by high speed competitive production. Smaller machines frequently could not make satisfactory welds at all.

A primary object of our invention, therefore, is to provide a process for the production of phosphate coatings of the Bonderized type on zinc surfaces, and in particular on galvanized steel and iron sheets, which while retaining all of the advantages of the previously used coatings can, in addition, be readily spot welded.

In general, this object of our invention is achieved through the application of our discovery that there is a maximum weight of coating which can be readily spot welded. From this follows another object of our invention, which includes the provision of a method for producing coatings of this character, and a coating composition by which the desired results may be achieved.

As the result of extensive investigation we have discovered the relative proportions of the

various ingredients, and the conditions of treatment in the treating bath which will consistently produce coatings below this maximum value, but which will still be above the minimum weight of coating necessary to give the desired paint service characteristics.

Our invention makes possible the application of such coated materials, having the combined advantages of the corrosion resistance of zinc and the superior paintability and paint holding properties resulting from the coating, to many uses hitherto impossible because of the impossibility of satisfactorily spot welding such materials.

By controlling the treatment in the manner to be described we limit the weight of coating to 0.030 oz. per sq. ft., which we have discovered to be the practical maximum which can be spot welded satisfactorily on good commercial equipment. We prefer, however, to maintain the coating weight lower than this value and even approaching 0.015 oz. per sq. ft. in order to make the material readily spot weldable even on somewhat inferior equipment. Below 0.015 oz. the paint preserving properties of the coating begin to be impaired. The range 0.030 to 0.015 is satisfactory as a good combination of these two properties, and in practice we prefer to operate at around 0.025 oz. per sq. ft. The coating weights given herein include the weight of the coating on both sides of one square foot of material.

Attempts to obtain light coatings within this range by merely diluting the commonly used solutions, shortening the time of treatment, or lowering the temperature of treatment have not been productive of satisfactory results. The coatings resulting from the practice of such expedients are of non-uniform thickness over the sheet, are poorly adherent and have otherwise unsatisfactory physical properties.

We have found it possible to produce consistently a light weight coating within the limits of this range on conventional galvanized coatings by using a solution within the following composition ranges:

Nitrate	per cent.	0.65 to 1.10
Free acid	points	1.5 to 4.0
Total acid	do.	16.0 to 25.0
Zinc	per cent.	0.35 to 0.70
Iron (ferrous)	do.	0.10 to 0.25

The acid concentration in "points" is a measure arrived at by titrating a 10 ml. sample of the solution with 0.1 normal sodium hydroxide.

The number of points are equal to the number of milliliters of sodium hydroxide necessary to produce the color change of the indicator. The indicator used for determining "free acid" was methyl orange, and that used for determining "total acid" was phenolphthalein.

Since for best all around results we prefer to keep the weight of coating near the middle of the permissible range, we prefer to use a solution within a somewhat more limited composition range, as follows:

Nitrate	per cent.	0.68 to 1.08
Free acid	points	2.0 to 3.4
Total acid	do	18.0 to 24.6
Zinc	per cent.	0.38 to 0.65
Iron (ferrous)	do	0.14 to 0.20

A particular solution composition within these ranges which we have found to result approximately in our preferred weight of coating of around 0.025 oz. per sq. ft. on conventional galvanized coatings is as follows:

Nitrate	per cent.	0.93
Free acid	points	2.4
Total acid	do	22.1
Zinc	per cent.	0.45
Iron (ferrous)	do	0.15

In making up the original solutions, a convenient method of arriving at this specified composition is by the addition of appropriate amounts of phosphoric acid, zinc nitrate, and metallic iron to water; or the iron may be added as ferrous phosphate. It will be within the skill of a chemist to arrive at these compositions, as guided by these titration procedures.

As a guide to the maintenance of the bath at the proper composition during the passage of a large amount of material through it, it will be found that the addition of phosphoric acid will raise both the free and the total acid concentrations. The addition of zinc nitrate will increase the concentrations of zinc, nitrate and total acid. A convenient means of increasing the iron concentration is the addition of iron in finely divided form such as steel wool, which is soluble in the bath, or ferrous phosphate.

By way of comparison, the solution most commonly used before our discovery, and which was productive of coatings too heavy to spot weld satisfactorily, was approximately as follows:

Nitrate	per cent.	0.5 to 0.6
Free acid	points	4 to 6
Total acid	do	30
Zinc	per cent.	0.4
Iron (ferrous)	do	0.25

The important change, which made our controlled light weight of coating possible, resides in the increased nitrate concentration, together with the reduction in both free and total acids. The changes in the zinc and iron concentrations are only incidental since they are of practically no significance in affecting the weight or properties of the coating with the exception of appearance: i. e., the higher the iron concentration, the darker the color of the coating; the higher the zinc concentration, the lighter the color of the coating.

The time and temperature of treatment in our new bath must be controlled to give a uniform coating with the proper adherence and surface texture. A treatment of around 40 to 60 seconds at approximately 135° F. is preferred, although treatments up to 120 seconds have been used without exceeding the desired coating weight, since

longer treatment does not increase the weight of coating very rapidly. Treatments much less than approximately 20 seconds will result in an uneven coating. Temperatures between 115 and 145° F. are satisfactory but temperatures greatly in excess of this range, such as above 160° F. should be avoided on account of the formation of an excessive amount of sludge in the bath. At somewhat lower temperatures, such as below 100° F. a heavier coating of unsatisfactory texture is produced.

Additional treatments preceding or following the coating step described have been used in the case of the previous process for producing heavy coatings, and although forming no part of this invention, are equally applicable to our new process for the production of light coatings; for example, a chromic acid rinse may be added.

A machine which we have found to be well adapted to the application of our solutions is described in Finkbone et al., Patent No. 2,175,599, and the rubber wetting rolls described therein are particularly useful in assisting in the production of a uniform coating.

While we have used the term "sheet" herein, this is not to be considered as a word of limitation, and it will be understood that wherever this word has been used it includes the word "strip."

While we have mentioned herein certain compositions, concentrations, weights, temperatures and times, which we consider preferable, it will be clear that these are exemplary, and that we are not limited as to these factors otherwise than as pointed out in the claims which follow.

Having now fully described our invention, what we claim as new, and desire to secure by Letters Patent is:

1. A coating bath containing phosphoric acid for producing controlled light weight phosphate coatings on zinc surfaces in which nitrate is present within the range 0.65 to 1.10% and in which the free acid does not exceed 4.0 points and the total acid does not exceed 25.0 points.

2. A coating bath containing phosphoric acid for producing controlled light weight phosphate coatings on zinc surfaces in which nitrates are present within the range 0.65 to 1.10%, zinc is present in the range 0.35 to 0.70%, iron (ferrous) is present in the range 0.10 to 0.25%, and in which the concentration of free acid is within the range 1.5 to 4.0 points, and in which the concentration of total acid is within the range 16.0 to 25.0 points.

3. A coating bath containing phosphoric acid for producing controlled light weight phosphate coatings on zinc surfaces in which nitrates are present within the range 0.68 to 1.08%, zinc is present in the range 0.38 to 0.65%, iron (ferrous) is present in the range 0.14 to 0.20%, and in which the concentration of free acid is within the range 2.0 to 3.4 points, and in which the concentration of total acid is within the range 18.0 to 24.6 points.

4. A coating bath containing phosphoric acid for producing controlled light weight phosphate coatings on zinc surfaces in which nitrates are present in an amount substantially 0.93%, zinc is present in an amount substantially 0.45%, iron (ferrous) is present in an amount substantially 0.15%, and in which the concentration of free acid is substantially 2.4 points and the concentration of total acid is substantially 22.1 points.

5. A process of producing controlled light weight phosphate coatings on zinc surfaces

which includes the steps of treating said metal surfaces in a bath according to claim 1 for not less than 20 seconds and not more than 120 seconds at a temperature not less than 100° F. and not more than 160° F.

6. A process of producing controlled light weight phosphate coatings on zinc surfaces which includes the steps of treating said metal surfaces in a bath according to claim 1 for not less than 40 seconds and not more than 60 seconds at a temperature not less than 115° F. and not more than 145° F.

7. A process of producing controlled light weight phosphate coatings on zinc surfaces which includes the steps of treating said metal surfaces in a bath according to claim 1 for not less than 40 seconds and not more than 60 seconds at approximately 135° F.

8. A process of producing controlled light weight phosphate coatings on zinc surfaces which includes the steps of treating said metal surfaces in a bath according to claim 4 for not less than 40 seconds and not more than 60 seconds at approximately 135° F.

9. A process of producing controlled, light weight phosphate coatings on zinc surfaces which includes the steps of treating said metal surfaces in a bath according to claim 3 for not less than 40 seconds and not more than 60 seconds at approximately 135° F.

10. As an article of manufacture, a galvanized metal sheet capable of being spot welded and of receiving and retaining paint coatings, produced by treating a conventional galvanized metal sheet in the bath of claim 1 for substantially 20 to substantially 120 seconds at a temperature of from substantially 100° to substantially 160° F.

11. As an article of manufacture, a galvanized metal sheet capable of being spot welded and of receiving and retaining paint coatings, produced by treating a conventional galvanized metal sheet in the bath of claim 2 for substantially 20 to substantially 120 seconds at a temperature of from substantially 100° to substantially 160° F.

12. As an article of manufacture, a galvanized metal sheet capable of being spot welded and of receiving and retaining paint coatings, produced by treating a conventional galvanized metal sheet in the bath of claim 3 for substantially 20 to substantially 120 seconds at a temperature of from substantially 100° to substantially 160° F.

13. As an article of manufacture, a galvanized metal sheet capable of being spot welded and of receiving and retaining paint coatings, produced by treating a galvanized metal sheet in the bath of claim 4 for substantially 40 to substantially 60 seconds at approximately 135° F.

14. A coating bath for producing controlled, light weight phosphate coatings on the zinc surface of galvanized iron or steel, said coating being of a character to permit spot welding of the said iron or steel, said coating bath consisting of phosphoric acid and salts of metals in water solution and containing upon analysis nitrates within the range of 0.65 to 1.10%, zinc within the range of 0.35 to 0.70%, ferrous iron within the range of 0.10 to 0.25%, and showing upon titration with 0.1% normal sodium hydroxide solution a free acid content (as indicated by methyl orange) requiring 1.5 to 4.0 milliliters of the said sodium hydroxide solution for neutralization and a total acid content (as indicated by phenolphthalein) requiring 16.0 to 25.0 milliliters of said sodium hydroxide solution for neutralization.

15. As an article of manufacture, a galvanized metal sheet capable of being spot welded and of receiving and retaining paint coatings, produced by treating a conventional galvanized metal sheet in the bath of claim 14 for substantially 20 to substantially 120 seconds at a temperature of from substantially 100° to substantially 160° F.

NOBLE E. HAYS.
GEORGE R. HOOVER.
ALVA E. TAYLOR.