Patented Jan. 12, 1937

2,067,216

UNITED STATES PATENT OFFICE

2,067,216

METHOD OF COATING METAL

John S. Thompson, Detroit, and Herman J. Lodeesen, Berkley, Mich., assignors to The Patents Corporation, Detroit, Mich.

No Drawing. Application August 19, 1936, Serial No. 96,904

7 Claims. (Cl. 148—6)

This invention relates to coating metal and more particularly it relates to an improvement in methods by which a substantially integral coating is produced by chemical means upon a metal surface which is thereafter covered with a coat of paint, varnish, enamel or the like which dries or hardens over the chemical coat and is hereinafter referred to for brevity as a siccative coat.

It is known that various treatments will produce a substantially integral coat upon metal by chemical changes in the surface of the metal which result in firmer adherence of a siccative coat thereto than can be obtained by direct application of the siccative coat upon bare metal. This has been practiced to a considerable extent, particularly with iron and steel, by the production on iron and steel of a phosphate coating as a foundation or bond for paint or the like. Similar phosphate coats may be produced upon zinc or magnesium, and by somewhat similar treatments substantially insoluble salts of the metals may be produced by treatment with organic acids including the dicarboxylic and hydroxy-dicarboxylic acids of the aliphatic series, and carboxylic acids having but one carboxyl group, and sulphonic acids of the aromatic series, particularly where oxidizing agents and copper compounds or the like are employed as accelerators. By proper manipulation, such salt coatings can be produced not only upon iron and zinc, but also upon tin, lead and copper. These various coatings, when formed so that they are firmly adherent and substantially integral coatings upon the metal, greatly increase the adherence of siccative coats to the metal. Also proper chemical treatment produces oxide coats on substantially all metals, and siccative coats adhere to such oxide coats better than to the bare metal. Similar increased adherence may be secured on aluminum by a coating of lithium aluminate or aluminum fluoride. The nitrous acid radical generally added to the solutions in the form of soluble nitrites such as sodium nitrite, generally facilitates the production of oxide coatings on metal and also the production of integral salt coats of the kind described above. These various bonding coats are hereinafter referred to for brevity as chemical coats.

While the adherence of siccative coats to the metal is greatly increased by the bonding effect of a chemical coat, it has been found difficult to avoid blisters between the chemical coat and the siccative coat where the chemical coat has been produced with the aid of the nitrous acid radical particularly when the finished surface is subjected to humidity tests.

The object of the present invention is to provide an intermediate treatment after the production of the chemical coat by means of a solution containing the NO_2 radical and before the application of the siccative coat, whereby this blistering under the siccative coat is minimized or eliminated.

After the production of the chemical coat, the surface is customarily washed before the application of the siccative coat. In accordance with the present invention, the chemical coat is preferably rinsed in the usual manner and is then treated with a dilute solution of chromic acid, phosphoric acid or oxalic acid. Treatment with dilute solutions of other acids, with a few exceptions such as nitric acid, reduces to some extent the blistering but not as effectively and satisfactorily as the acids named. A treatment in a dilute solution of nitric acid seems to increase rather than decrease the blistering.

The three acids named above are preferred in the order in which they are named, the chromic acid being decidedly preferable, phosphoric acid being next in efficiency, and oxalic acid being not so desirable but still effective to materially reduce the blistering.

In the preferred form, the chromic acid solution is formed by introducing from 2 grams to 20 grams of chromic acid in a gallon of water. For ordinary commercial purposes about 4 grams of chromic acid to a gallon of water is preferred, but fairly good results may be obtained with a dilution as great as 2 grams in a gallon of water, and while a strength greater than 4 grams to a gallon of water seems unnecessary, it seems to do little, if any, harm until 20 grams or over are used. Stronger solutions of chromic acid are likely to injure the chemical coat, and even with 20 grams to the gallon, undesirable yellow streaks develop, although these streaks do not seem to affect the adherence of the siccative coat.

It is preferable to employ the customary rinsing after the production of the chemical coat and before the use of the chromic acid rinse, so as to avoid contamination of the chromic acid rinse. No treatment is necessary after the chromic acid rinse and before the application of the siccative coating. If any subsequent rinsing takes place, it should be with distilled water or at least with water which does not contain lime, alkali or other material which may result in contaminating the chemical coat sufficiently to produce blisters.

The length of treatment in the chromic acid rinse depends upon the strength of the solution employed, the condition of the work and the tem-

perature of the rinsing bath. Preferably the bath is employed at a temperature approaching the boiling point and, with the strength mentioned, one minute or less in the bath is ordinarily sufficient.

When phosphoric acid rinse is employed, it may be used hot in a solution having a strength which requires between ¼ cc. and ½ cc. tenth normal caustic soda to neutralize 10 cc. of the rinse water, methyl orange being the indicator. Where this rinse water is employed over a phosphate chemical coat, it gradually becomes contaminated with phosphates and is not effective where the phosphate builds up so that it requires more than four times as much alkali to neutralize a given amount of solution with phenolphthalein as an indicator than it does to neutralize the same amount of solution with methyl orange as an indicator. About one minute treatment in such a phosphoric acid rinse is ordinarily sufficient.

Where an oxalic acid rinse is employed, it should be used hot in approximately corresponding strength to that indicated above for the phosphoric acid solution.

The acid rinse to minimize or eliminate blisters under a siccative coat is particularly effective when employed with a chemical coat produced by a phosphate solution containing the nitrous acid radical NO_2, but is also effective with the other chemical coats mentioned above which are obtained on metallic surfaces by means of solutions containing the NO_2 radical. Also, while the most important use of the method at the present time is in connection with coating iron or steel, it is also effective with the chemical coats produced upon other metals, as mentioned above.

It is understood that in the rinses of this invention other ingredients may be present besides the chromic, oxalic and phosphoric acids; for example, mixtures of any of these may be used, although substantially pure, dilute, aqueous solutions of these acids are preferably employed.

After the rinse of this invention the metallic surfaces are either air-dried or heat-dried before application of the siccative coat.

What we claim is:

1. The method which consists in forming on a surface of metal by means of a solution containing the NO_2 radical a chemical coat of the group consisting of coatings on metal of oxide of the metal coated, on iron, steel, zinc and magnesium, of substantially insoluble phosphates, on iron, steel, zinc, magnesium, tin, lead and copper, of a substantially insoluble salt of an acid in the group consisting of the dicarboxylic and hydroxy-dicarboxylic acids of the aliphatic series and carboxylic acids having but one carboxyl group and sulphonic acids of the aromatic series, and, on aluminum, lithium aluminate and aluminum fluoride, rinsing the chemical coat with a substantially pure dilute aqueous solution of an acid in the group consisting of chromic acid, phosphoric acid and oxalic acid and mixtures thereof, and covering the rinsed chemical coat with a siccative coat.

2. The method which consists in producing on a metallic surface a phosphate-containing coating by means of a solution containing the NO_2 radical, and after the coating operation thereafter rinsing the coated surface in a dilute aqueous solution of chromic acid.

3. A method in accordance with claim 1 in which the dilute acid rinse is a chromic acid rinse, of the strength of 2 to 20 grams of chromic acid per gallon of water.

4. A method in accordance with claim 1 in which the acid rinse is of oxalic acid requiring between ¼ cc. and ½ cc. tenth normal caustic soda to neutralize 10 cc. of the solution, methyl orange being the indicator.

5. A method in accordance with claim 1 in which the acid rinse is a solution of phosphoric acid requiring between ¼ cc. and ½ cc. tenth normal caustic soda to neutralize 10 cc. of the solution, methyl orange being the indicator, and requiring not more than four times as much alkali to neutralize a given amount of the solution with phenolphthalein as an indicator than with methyl orange as an indicator.

6. The method which comprises treating a metal surface carrying a chemical coating produced by the action of a solution containing the NO_2 radical, with a substantially pure dilute aqueous solution of one of the group consisting of chromic acid, phosphoric acid, oxalic acid, and mixtures thereof.

7. The method which comprises treating a surface of iron or steel carrying a chemical coating containing phosphate produced by the action of a solution containing the NO_2 radical, with a dilute aqueous solution of chromic acid.

JOHN S. THOMPSON.
HERMAN J. LODEESEN.

CERTIFICATE OF CORRECTION.

Patent No. 2,067,216. January 12, 1937.

JOHN S. THOMPSON, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 18, claim 2, strike out the words "after the coating operation"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of March, A. D. 1937.

Henry Van Arsdale
Acting Commissioner of Patents.

(Seal)