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3,432,270

METHOD FOR DETERMINING NITRITE CONCENTRATION IN ACIDIC ACCELERATED PHOSPHATING SOLUTIONS**Ferdinand P. Heller, Philadelphia, Pa., assignor to Amchem Products, Inc., Ambler, Pa., a corporation of Delaware**

No Drawing. Filed July 25, 1966, Ser. No. 567,405

U.S. Cl. 23—230

2 Claims

Int. Cl. G01n 33/00

ABSTRACT OF THE DISCLOSURE

This invention relates to the art of producing phosphate coatings on metal surfaces by means of acidic accelerated phosphating solutions containing at least a nitrite as an accelerating agent. The invention is particularly concerned with methods for determining the concentration of such nitrite in phosphating solutions. The invention finds its principal utility in the operation of phosphate coating solutions containing both chlorate and nitrite, although it is also useful with phosphate coating solutions containing nitrite and nitrate, and with solutions containing nitrite alone as the principal accelerating agent.

Nitrite has been used for many years as an accelerating agent, and for other functions, in acidic phosphate coating solutions. The quantity of nitrite in the solutions is desirably kept within certain concentration ranges during the course of use of the solution. This is accomplished by adding makeup nitrite to the solution, either continuously or periodically. The rate of addition of makeup nitrite is commonly determined by measuring the concentration of nitrite in the phosphating solution.

Heretofore, the nitrite concentration in the solutions has been determined by titrating a sample of the solution, by first acidifying it and then titrating against a standard solution with an indicator giving a color change at the end point. This prior method causes inconvenience to the relatively unskilled operators of the phosphate baths, because the solutions are turbid and the color change at the end point may be masked.

The foregoing inconvenience has been tolerated by the art for some time. However, recently there have been introduced extremely commercially useful acidic phosphating solutions in which both nitrite, and another oxidizing agent, chlorate, are used as accelerators. The monitoring of nitrite concentration in these new solutions is a much more difficult problem for the unskilled operator of the phosphate coating bath. The conventional titrating system outlined above is not useful. The reason for this is that the chlorate in the solution is capable, when the solution is strongly acidified, of oxidizing the nitrite to nitrate. Thus if one attempts to titrate for nitrite in the conventional manner he destroys the nitrite for which he is titrating in the preparatory step of acidifying the sample. Oxidizing agents, other than chlorate, which are capable of oxidizing nitrite to nitrate, will, if present in the sample, cause the same problem.

Skilled chemists can resort to other, more sophisticated means for determining nitrite in the presence of chlorate, of under conditions where the standard titration system is unreliable. However, such techniques are of little assistance to the relatively unskilled personnel commonly charged with successfully applying phosphate coatings to metal by means of phosphating solutions.

The principal object of the present invention is to provide a simple, easily used method for determining the quantity of nitrite in phosphate coating solutions, especially when chlorate is also present in said solutions.

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A related object of the invention is to provide a nitrite determination method, the operation of which is well within the skill of the operators charged with maintaining the coating producing quality of phosphating baths during the course of their use.

Nitrite accelerated coating solutions of the kind being discussed may contain from as little as 0.01–0.03 gram/liter of nitrite to as much as 1.0 gram/liter or even more. In general, the concentration of nitrite will be about 0.015 gram/liter of 0.15 gram/liter. Nitrite in all cases discussed herein is calculated as NO_2 .

The present invention resides in my discovery that solid sulfamic acid, when introduced into a nitrite accelerated phosphating bath, causes quantitative decomposition of the nitrite. Gaseous nitrogen is a decomposition product, and the quantity of nitrogen evolved is proportional to the amount of nitrite originally present. The evolved nitrogen can be collected and measured. Such measurement provides a number readily convertible to nitrite concentration.

It has been known that sulfamic acid reacts with nitrite under some conditions. However, when I attempted to react aqueous solutions of sulfamic acid with nitrite in phosphate coating solutions containing chlorate or other oxidants which oxidize nitrite to nitrate to obtain nitrogen, I found that no reaction took place. This indicated that the conditions present in phosphate coating solutions made the sulfamic acid-nitrite reaction unavailable as an analytical tool. However, I found that when solid sulfamic acid is introduced into a nitrite containing phosphating solution, nitrogen is quantitatively evolved. This discovery was totally unexpected in view of the failure of aqueous sulfamic acid to react. The reasons for obtaining a successful reaction with solid sulfamic acid, in the face of the inertness of even saturated sulfamic acid solutions in the same environment, are not understood.

The procedures for performing the methods of the invention are quite simple. A suitable closable vessel for holding the sample to be analyzed is employed. One such vessel is a simple fermentation flask. It is preferred that the vessel have a part or an attachment for collection of the evolved nitrogen. Thus, when a fermentation flask is used, the tip may be cut off and a tapered calibrated tube, such as a centrifuge tube, fitted onto the flask in inverted position. Those skilled in the art can devise other effective gas collection means, and it should be understood that when the term "gas collection tube" is used in the claims which follow, the term is being employed in a broad sense to include such means.

The vessel for the sample is completely filled with liquid so that no air bubbles remain. The quantity of liquid thus placed in the vessel will therefore be standard from sample to sample, and once known, provides a basis for concentration calculations and for calibration of the gas collecting tube or means if that is desired.

In accordance with the preferred procedure, solid sulfamic acid is then added to the sample containing vessel in an amount in excess of that required to react with the maximum quantity of nitrite expected to be present in the sample. For nitrite containing solutions having concentrations in the ranges commonly employed in phosphating solutions, approximately 5 grams of sulfamic acid meets this requirement for a sample of approximately 40 milliliters. The closable sample vessel is then closed, as by placing a finger over the opening therein, and the sulfamic acid is mixed with the solution by agitating the vessel gently. This can be done readily by inverting the vessel once or more.

Upon the mixing of the sulfamic acid with the sample, nitrogen is evolved. The vessel is righted or otherwise placed so that the nitrogen will collect in the gas collec-

tion tube or gas collecting means in communication with the vessel. After a short period of time, such as one or two minutes, the amount of gas in the collection tube is observed and the thus observed value is used to calculate the quantity of nitrite. (One mol of nitrogen gas, 22.4 liters, corresponds to one mol of nitrite.) For the convenience of phosphate bath operators, who are rarely skilled chemists, the gas collection tube may be calibrated in grams/liter of nitrite, or in other calibrations meaningful to the operator, such as pounds/gallon of nitrite makeup solution required to restore the desired nitrite level in the bath.

I claim:

1. A method for determining the concentration of nitrite in acidic accelerated phosphating solutions comprising mixing solid sulfamic acid with a sample of the phosphating solution to be analyzed, thereby evolving nitrogen gas in an amount proportional to the quantity of nitrite present in the sample, collecting the evolved nitrogen gas, and measuring the quantity of evolved nitrogen.

2. A method for determining the concentration of nitrite in acidic phosphating solutions containing both chlorate and nitrite comprising filling a closable vessel having a gas collection tube in communication therewith with a sample of the phosphating solution to be analyzed,

adding solid sulfamic acid to the sample in said vessel in an amount in excess of that required to react with the maximum quantity of nitrite expected to be present in the sample, closing said vessel and mixing said sample with said solid sulfamic acid therein, thereby evolving nitrogen gas in an amount proportional to the quantity of nitrite present in the sample, collecting the evolved nitrogen gas in said gas collection tube, and measuring the quantity of evolved nitrogen gas collected in said tube.

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U.S. Cl. X.R.

252—408