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PHOSPHITE TESTING METHOD

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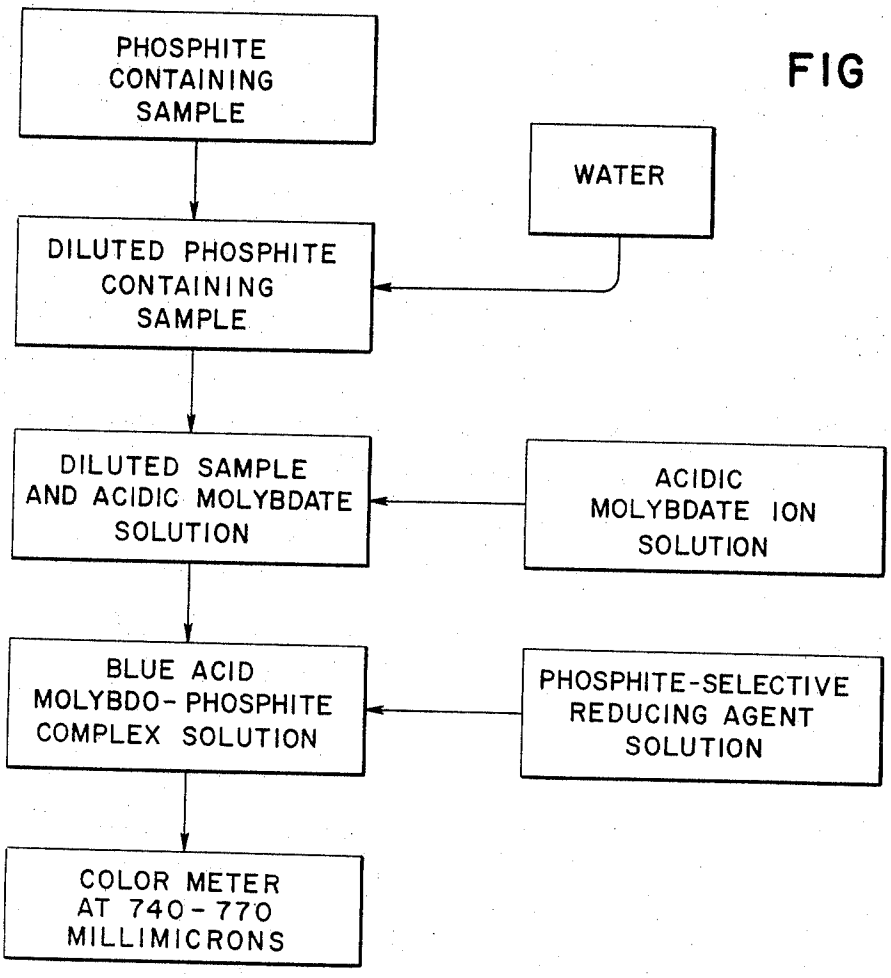


FIG 1

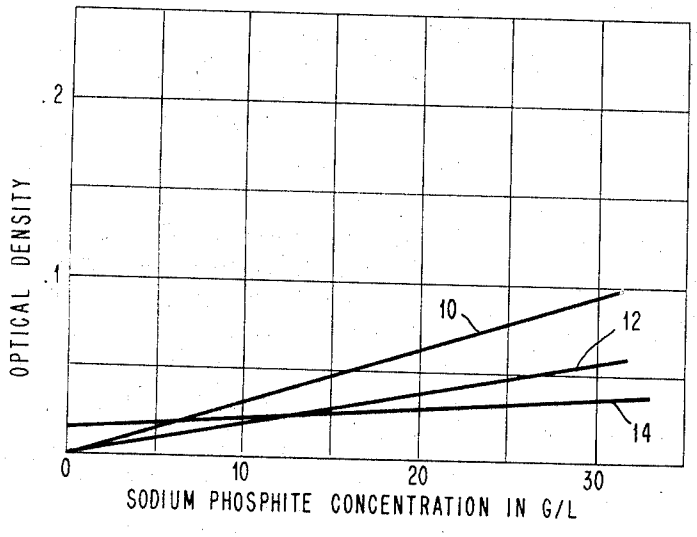


FIG. 2

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PHOSPHITE TESTING METHOD

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ABSTRACT OF THE DISCLOSURE

A testing method for determining the phosphite ion content of a sample in which hypophosphite ion is also present by adding to the to-be-tested sample an acid buffered metal anion solution capable of forming colored heteropoly acids with phosphorous-containing compounds and then adding a phosphite ion selective reducing agent. The intensity of the resulting colored heteropoly phosphite complex is then measured by colorimetry and the measured intensity compared with a standard to determine phosphite content of the sample.

This invention relates to a method for determining the phosphite content of a sample solution, and more particularly to a method for obtaining the phosphite content of a solution wherein hypoyphosphite ion is also present.

The electroless deposition of metallic layers of a wide variety of metals is known in the art. The mechanism of the reaction is based on a chemical added to the plating solution which acts as a reducing agent for the metal being plated. In electroless plating, the metal ion in solution is reduced to the corresponding metal by gaining the required number of electrons. The source of these electrons is the oxidation of a reducing agent in the plating solution which generally in the art is hypophosphite ion. The electroless plating process has the obvious advantage over electroplating in that the substrate on which the metal is deposited need not be a conductive one. The replenishment of the hypophosphite ion and metal ions to the electroless bath would appear to be all that would be necessary to operate the electroless bath over long periods of time. Actually, this is not the case, because the hypophosphite ion is oxidized in the reaction almost quantitatively to the phosphite ion. Metal phosphites tend to have low solubility values. When precipitation of the metal phosphite takes place in the form of a finely dispersed solid, the particles act as catalytic nuclei for a spontaneous bath decomposition. Bath decomposition represents, of course, a heavy loss in materials. However, the greatest problem caused by the decomposition is that the entire plating equipment is coated with the metal being deposited. This results in a stoppage in the operation for a thorough cleanout of the entire system. The problem of bath stability has been combated in the prior art by putting additives in the bath which tends to increase the bath stability and by disposing of the bath materials at a point in time well before the bath stability is in question.

The time at which the electroless plating bath is disposed of has been rather arbitrarily and empirically determined. This practice has necessarily wasted large volumes of chemical material by early dumping of the electroless plating baths. Further, since the time of dumping is arbitrary, plate-out has occurred on many occasions nevertheless. The difficulty has been the inavailability of a suitably rapid test method for determining the phosphite content of the electroless plating bath. Up until the present time there has been no method for both accurately and rapidly determining the phosphite content of a solution containing both phosphite and hypophosphite ion. In a solution, such as an electroless plating bath, containing

both phosphite and hypophosphite ions there has always been interference from the hypophosphite and other solution constituents, and the resulting phosphite content values for the solution are inaccurate and meaningless due to the interference.

It is an object of this invention to provide a method for determining the phosphite content of the sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite ion or other solution constituents.

It is another object of this invention to provide a test method that uses a reducing agent which reacts preferentially with the phosphite ion without undue interference from the hypophosphite ion to form a soluble colored complex solution, which solution has a color intensity according to the phosphite content of the solution.

It is a further object of this invention to provide a test method which utilizes colorimetric procedures for continuously determining the phosphite content in an electroless plating bath solution by use of a reducing agent which reacts preferentially with the phosphite ion without interference from the hypophosphite ion to form a soluble colored complex.

These and other objects are accomplished in accordance with the broad aspects of the present invention by providing selective reducing agents which react with the phosphite ion complex in a solution at a faster rate of reaction than they do with the hypophosphite ion in the solution. The sample solution to be tested is mixed with an acid buffered solution containing metallic anions capable of forming heteropoly acids with phosphorus and a phosphite ion selective reducing agent solution. A colored heteropoly phosphite soluble complex is formed almost instantaneously. The intensity of the colored solution is measured by colorimetric means within a short period of time after the addition of the reducing agent. The measured color intensity is compared with a standard to determine the phosphite content of the sample solution.

The entire analysis can be performed within a period of four to five minutes. The prior analysis of phosphites in the presence of hypophosphite has been by difference, involving extremely lengthy procedures with poor accuracy. The test method is accurately operable with high or low concentrations of hypophosphite ion present.

The foregoing and other objects, features and advantages of the present invention will be apparent from the following more particular description of the preferred embodiments of the invention as illustrated in the accompanying drawings.

In the drawings:

FIGURE 1 is a flow diagram illustrating the method for determining the phosphite content of a solution; and

FIGURE 2 shows standard optical density versus phosphite ion concentration for four different phosphite ion selective reducing agents.

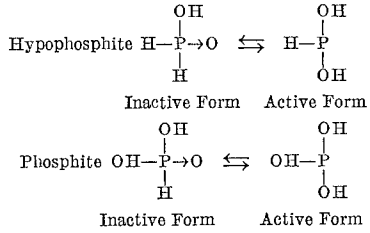
Referring now to the flow diagram of FIGURE 1, a sample of phosphite containing solution is diluted with a known amount of water. A solution of molybdate ion in a non-oxidizing and non-reducing acid is formed by mixing, for example, sodium molybdate with concentrated sulfuric acid. The concentration of the molybdate ion is only critical in that there is an excess of the ion for the subsequent reaction. The acidic molybdate ion solution is then added to the diluted phosphite containing sample solution and thoroughly mixed therewith. This mixture is then placed in a reaction zone or vessel and a phosphite ion selective reducing agent solution is added thereto. Useful phosphite ion selective reducing agents are ascorbic acid, isoascorbic acid, hydroquinone and p-methylaminophenol sulfate. The solutions in the reaction zone are thoroughly mixed and almost instantaneously a blue-

colored molybdophosphite soluble complex solution is formed. The intensity of the blue-colored solution is measured on a colorimeter at a suitable wavelength which is preferably between approximately 740 to 770 millimicrons. The measurements should be made within approximately two minutes and preferably within 30 seconds after the addition of the reducing agent because the reducing agent in the solution will with time start to react with the hypophosphite ion in solution and thereby cause interference. The measured color intensity is then compared with a standard to determine the precise phosphite content of the sample solution. FIGURE 2 gives typical standard optical density vs. phosphite ion concentration curves using a Technicon Autoanalyzer colorimeter for ascorbic acid, isoascorbic acid, hydroquinone and p-methylaminophenol sulfate. The curve **10** is for both ascorbic and isoascorbic acids. The curves **12** and **14** are for, respectively, hydroquinone and p-methylaminophenol sulfate.

The non-oxidizing and non-reducing acid in the solution is important. The concentrated acid is used to buffer the reaction and to further retard the reaction of the interfering hypophosphite ions. The normality of the acid solution added should be above approximately 4.0 normal and preferably between 4 and 6 normal. The use of an acid having a normality of, for example, 2.5 will allow interference from the hypophosphite ions in solution.

The test method lends itself to a continuous testing operation. A manifold has been made which, together with a proportioning pump, is capable of continuously mixing and reacting the various solutions in the desired manner. The finally reacted solution is then continuously passed to any conventional colorimeter wherein the intensity of the blue-colored solution is continuously measured and recorded on a standard recording device. In this manner, for example, the phosphite concentration of an electroless plating bath may be continuously monitored and when the danger level of phosphite ion in the solution is reached, the electroless plating bath may be discarded.

The theory of operation of the present invention may be more readily understood by observing that the hypophosphite and phosphite ions exist in tautomeric forms:



Orthophosphorous acid, H_3PO_3 and phosphite ion, forms a heteropoly acid with molybdate solution based on six molybdenum atoms. Hypophosphorous acid, H_3PO_2 and hypophosphite ion, also forms a heteropoly acid with molybdate solution based on six molybdenum atoms. Phosphoric acid, H_3PO_4 and phosphate ion, forms a heteropoly acid with molybdate solution based on either nine or twelve molybdenum atoms with the phosphorus atom at the center. The heteropoly molybdenum complex of orthophosphite may be called molybdophosphite and the hypophosphite complex called molybdohypophosphite and that of the phosphate, molybdophosphate. The reason that the method for analyzing phosphite in the presence of large quantities of hypophosphite works without interference from the hypophosphite is that there is a difference in the rate of reaction of the two molybdo complexes. The rate of reaction of the molybdophosphite complex is somewhat faster than that of the molybdohypophosphite when there is used a phosphite ion selective reducing agent such as ascorbic acid, isoascorbic acid, hydroquinone or p-methylaminophenol sulfate. The reaction is unique because the usual situation is that the reducing agent will reduce the hypophosphite complex faster than the phosphite complex to form heteropoly blue or molybdenum blue complexes. On this basis there have been test method in the prior art to determine hypophosphite concentration in a solution without interference from the phopshite ion.

The following examples are included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit of the invention.

EXAMPLE 1

A series of sample solutions with known phosphite ion and hypophosphite ion concentrations, as given by their weight expressed as sodium phosphite and sodium hypophosphite, were tested according to the flow diagram of FIGURE 1. The sample solution in each case was diluted in the ratio of one part sample solution to 13.2 parts water by volume. A 10 percent by weight sodium molybdate solution in 5 normal sulfuric acid was made up. The diluted sample solution was mixed in the ratio of one part sample solution to 1.55 parts acidic molybdate ion solution by volume. The diluted sample and acidic molybdate solution mixture was placed in a reaction zone. A 10 percent by weight isoascorbic acid aqueous solution was freshly made. The isoascorbic acid solution was mixed with the diluted sample and acidic molybdate solution in the ratio of one part sample and acidic molybdate solution to 1.64 parts isoascorbic acid solution. The optical densities of the resulting blue-colored solution was measured at 762 millimicrons in a Technicon Autoanalyzer colorimeter within 2 minutes after the addition of the isoascorbic acid solution to the sample and molybdate solution. The concentrations and results are tabulated in Table I.

TABLE I

Concentration Hypophosphite-Phosphite in grams/liter	Optical Density	Concentration Hypophosphite-Phosphite in grams/liter	Optical Density	Concentration Hypophosphite-Phosphite in grams/liter	Optical Density
0-0	.003	12-0	.003	24-0	.003
0-10	.032	12-10	.032	24-10	.032
0-20	.061	12-20	.061	24-20	.061
0-30	.089	12-30	.089	24-30	.089
0-40	.104	12-40	.102	24-40	.106

It is observed from the Table I that the phosphite content can be determined without interference from the hypophoshpite using this colormetric technique since the optical density is shown to be, with only minor exceptions, identical regardless of the hypophosphite ion concentration in the sample solution. The phosphite concentration versus optical density obtained in this example is plotted as curve 10 for sodium phosphite concentrations of 10, 20 and 30 grams per liter.

EXAMPLE 2

The Example 1 was repeated on a series of sample solutions with the sole exception that a 10 percent by weight ascorbic acid solution was used in place of the isoascorbic acid solution of Example 1. The concentrations and results are given in the Table II.

TABLE II

Concentration Hypophosphite-Phosphite in grams/liter	Optical Density	Concentration Hypophosphite-Phosphite in grams/liter	Optical Density	Concentration Hypophosphite-Phosphite in grams/liter	Optical Density
0-0	.003	12-0	.003	24-0	.003
0-10	.032	12-10	.032	24-10	.032
0-20	.061	12-20	.061	24-20	.069
0-30	.089	12-30	.089	24-30	.089
0-40	.105	12-40	.104	24-40	.104

The Table II results indicate the preferential phosphite ion selective reducing agent, ascorbic acid, is effective in determining the phosphite composition regardless of the concentration of the hypophosphite ion in the solution. The phosphite concentration versus optical density is substantially identical regardless whether isoascorbic acid or ascorbic acid is used. The curve 10 of FIGURE 2 applies to both isoascorbic acid and ascorbic acid.

EXAMPLE 3

A series of sample solutions of known phosphite ion and hypophosphite ion concentrations were tested according to the procedure of Example 1. The phosphite ion selective reducing agent was, however, in this Example, a 10 percent by weight hydroquinone aqueous solution. The concentrations and results are given in Table III.

TABLE III

Concentration hypophosphite-phosphite in grams/liter:	Optical density
0–10	.018
0–20	.037
0–30	.055
30–0	.003
10–20	.036
20–30	.055

The results show that hydroquinone is an effective phosphite ion selective reducing agent for the present test method. The phosphite concentration versus optical density obtained in this example is plotted as curve 12 for sodium phosphite concentrations of 10, 20 and 30 grams per liter.

EXAMPLE 4

The Example 1 procedure was repeated upon a series of sample solutions, except that a 10 percent by weight p-methylaminophenol sulfate aqueous solution was used in place of the isoascorbic solution. The concentrations and results are given in Table IV.

TABLE IV

Concentration hypophosphite-phosphite in grams/liter:	Optical density
0–10	.022
0–20	.029
0–30	.036
30–0	.014
20–10	.021
20–30	.038

The results show that p-methylaminophenol sulfate is an effective phosphite ion selective reducing agent for the present test method. The phosphite concentration versus optical density obtained in this example is plotted as curve 14 for sodium phosphite concentrations of 10, 20 and 30 grams per liter.

The examples have shown that the molybdate anion is effective in the present test method to form a colored heteropoly molybdo-phosphite soluble complex that can be used with the aid of colorimetric analysis to determine the phosphite concentration of the sample solution. Comparable results can be obtained using other metallic anions capable of forming heteropoly acids with phosphorus, such as the tungstate, vanadate and chromate anions. Mixture of these metallic anions with or without the molybdate anion can also be used. The characteristics and chemistry of these heteropoly acids of phosphorus is more fully described "Phosphorus and Its Compounds" by John R. Van Wazer, published by Interscience Publishers, Inc., New York, N.Y., 1958, volume I, pp. 385, 559–569.

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art

that the foregoing and other advantages in form and detail may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. The method for determining the phosphite content of a sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite comprising:

placing the said sample solution in a mixing and reaction zone;

mixing with said sample solution in said mixing and reaction zone a solution containing metallic anions capable of forming heteropoly acids with phosphorous, said solution having a pH in a range which retards the reaction of hypophosphite ions with said metallic anions and then adding a phosphite ion selective reducing agent solution to react with said phosphite ion and produce a colored heteropoly phosphite soluble complex solution;

measuring the intensity of the colored solution prior to the reaction of the hypophosphite ion with the selective reducing agent; and

comparing the measured color intensity to a standard to determine the phosphite content of said sample solution.

2. The method of claim 1, wherein the intensity of the colored heteropoly phosphite soluble complex is measured within approximately two minutes after the addition of said phosphite ion selective reducing agent to the mixing and reaction zone.

3. The method for determining the phosphite content of a sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite comprising:

placing the said sample solution in a mixing zone;

mixing with said solution in said mixing zone an acidic solution containing metallic anions capable of forming heteropoly acids with phosphorus, said solution having a pH in a range which retards the reaction of hypophosphite ions with said metallic anions;

passing the said sample solution and said acidic solution from said mixing zone into a reaction zone;

passing a phosphite ion selective reducing agent solution into the said reaction zone to react with said phosphite ion and produce a colored heteropoly phosphite soluble complex solution;

measuring the intensity of the colored solution prior to the reaction of the selective reducing agent with the hypophosphite ion; and

comparing the measured color intensity to a standard to determine the phosphite content of said sample solution.

4. The method of claim 3, wherein the acidic solution in which the metallic anions are dissolved is of a non-oxidizing and non-reducing type, and wherein the intensity of the colored heteropoly phosphite soluble complex is measured within approximately two minutes after the addition of said phosphite ion selective reducing agent to the said reaction zone.

5. The method of claim 4 wherein the said phosphite ion selective reducing agent is ascorbic acid.

6. The method of claim 4 wherein the said phosphite ion selective reducing agent is isoascorbic acid.

7. The method of claim 4 wherein the said phosphite ion selective reducing agent is hydroquinone.

8. The method of claim 4 wherein the said phosphite ion selective reducing agent is p-methylaminophenol sulfate.

9. The method of claim 4 wherein the said metallic anions are tungstate anions.

10. The method of claim 4 wherein the said metallic anions are chromate anions.

11. The method of claim 4 wherein the said metallic anions are molybdate anions.

12. The method of claim 4 wherein the said metallic anions are vanadate anions.

13. The method of claim 12 wherein the said phosphite ion selective reducing agent is ascorbic acid.

14. The method of claim 12 wherein the said phosphite ion selective reducing agent is isoascorbic acid.

15. The method of claim 12 wherein the said phosphite ion selective reducing agent is hydroquinone.

16. The method of claim 12 wherein the said phosphite ion selective reducing agent is p-methylaminophenol sulfate.

17. The method for determining the phosphite content of a sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite comprising:

placing the said sample solution in a mixing zone;

mixing with said solution in said mixing zone a solution of molybdate ion in approximately 4.0 to 6.0 N sulfuric acid;

passing the said sample solution and said molybdate ion solution from said mixing zone into a reaction zone;

passing a phosphite ion selective reducing agent solution into the said reaction zone to react the said phosphite ion in said sample solution with said reducing agent and produce a blue-colored molybdophosphite soluble complex solution;

measuring the intensity of the blue-colored solution within approximately 30 seconds after the addition of the said reducing agent; and

comparing the measured color intensity to a standard to determine the phosphite content of said sample solution.

18. The method for determining the phosphite content of a sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite comprising:

placing the said sample solution in a mixing zone;

continuously passing into said mixing zone at a substantially constant rate a solution of molybdate ion in (highly concentrated) sulfuric acid solution; said solution having a pH in a range which retards the reaction of hypophosphite ions with said molybdate ion;

continuously passing at substantially a constant rate the said sample solution and said molybdate ion in sulfuric acid solution from said mixing zone into a reaction zone;

continuously passing a phosphite ion selective reducing agent solution into said reaction zone at a substantially constant rate to react with said phosphite ion in said sample solution and produce a blue-colored molybdophosphite soluble complex solution;

measuring the intensity of the blue-colored solution within approximately 30 seconds after the addition of the said reducing agent; and

comparing the measured color intensity to a standard to determine the phosphite content of said sample solution.

19. The method for determining the phosphite content of a sample solution containing both phosphite and hypophosphite ions without interference from the hypophosphite comprising:

placing the said sample solution in a mixing zone;

continuously passing into said mixing zone at a substantially constant rate a solution of sodium molybdate in approximately 4.0 to 6.0 N sulfuric acid;

continuously passing at substantially a constant rate the said sample solution and said sodium molybdate in sulfuric acid solution from said mixing zone into a reaction zone;

continuously passing a phosphite ion selective reducing agent solution into said reaction zone at a substantially constant rate to react with said phosphite ion in said sample solution and produce a blue-colored molybdophosphite soluble complex solution;

measuring the intensity of the blue-colored solution within approximately 2 minutes after the addition of the said reducing agent; and

comparing tthe measured color intensity to a standard to determine the phosphite content of said sample solution.

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U.S. Cl. X.R.

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