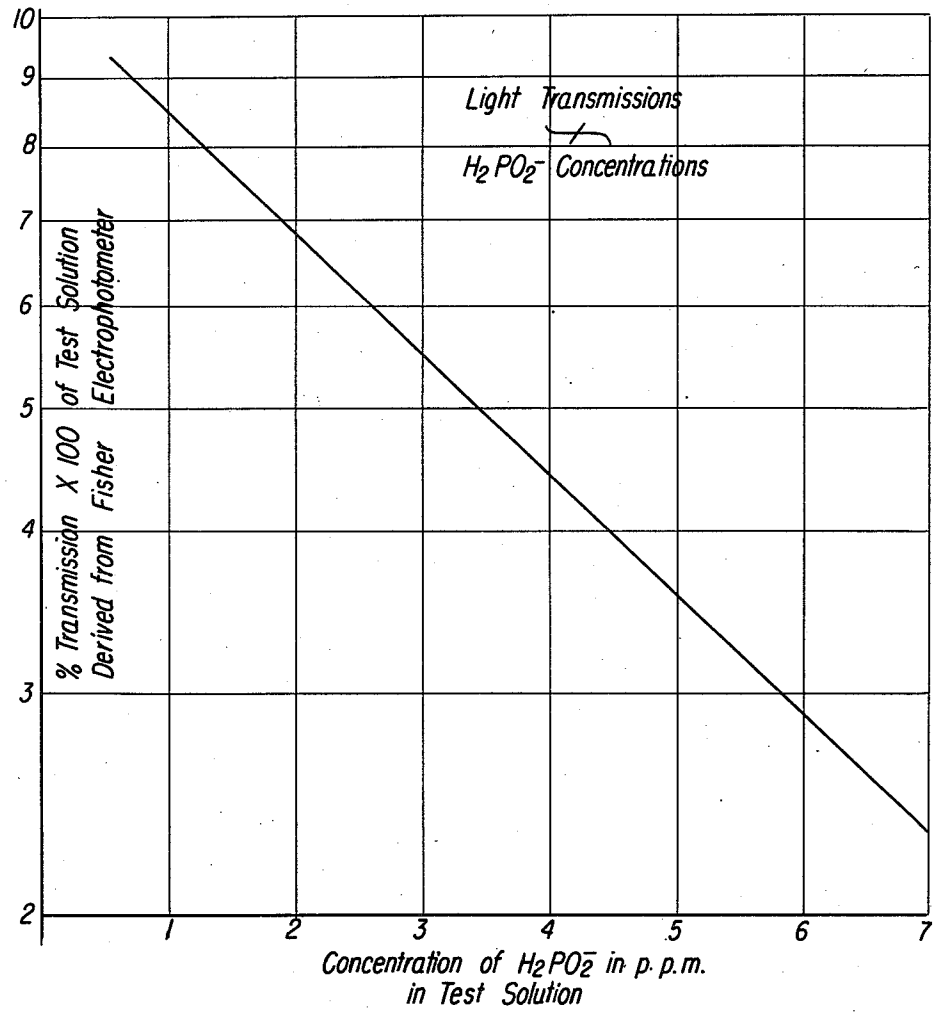
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COLORIMETRIC METHODS OF DETERMINING HYPOPHOSPHITE CONTENTS OF SOLUTIONS

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COLORIMETRIC METHODS OF DETERMINING HYPOPHOSPHITE CONTENTS OF SOLUTIONS

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The present invention relates to colorimetric methods of determining the hypophosphite anion concentrations or contents of sample solutions, particularly chemical nickel plating baths of the nickel cations-hypophosphite anion type. This application is a continuation-in-part of the copending application of Gregoire Gutzeit, Serial No. 287,207, filed May 10, 1952, now abandoned.

In the copending application of Paul Talmey and William J. Crehan, Serial No. 222,222, filed April 21, 1951, now Patent No. 2,658,839, granted November 10, 1953, there is disclosed a continuous chemical nickel plating process that employs a bath of the nickel cation-hypophosphite anion type; which process embraces the step of regenerating the bath as the ingredients thereof become exhausted. Specifically, in the bath, as the process is carried out, nickel cations are reduced to metallic nickel and deposited upon the object being plated, while hypophosphite anions are correspondingly oxidized to phosphite anions, whereby the bath becomes depleted in nickel cations and hypophosphite anions. In order to prevent undesirable depletion of the nickel cations and the hypophosphite anions in the bath, appropriate additions are made thereto either continuously or periodically for the purpose of regenerating the bath. Specifically, the hypophosphite anion concentration of the bath may be increased by the addition thereto of sodium hypophosphite. Now this step of regenerating the bath with reference to the addition of hypophosphite anions requires periodic testing or determination of the hypophosphite anion concentration or content thereof, which step has heretofore been carried out by a skilled chemist employing elaborate quantitative chemical analysis steps that are both very tedious and time-consuming.

Accordingly, it is a general object of the present invention to provide a simple, fast and expedient method of determining the hypophosphite concentration or content of sample solutions, and especially of chemical nickel plating baths of the nickel cation-hypophosphite anion type.

Another object of the invention is to provide a colorimetric method of determining the hypophosphite anion concentration or content of a sample solution.

Another object of the invention is to provide a colorimetric method of the character noted that involves a molybdenum-blue reaction.

A further object of the invention is to provide a colorimetric method of determining the hypophosphite anion concentration or content of a sample solution involving the molybdenum-blue reaction, that is sufficiently accurate for industrial purposes notwithstanding the presence in the sample solution of normally interfering phosphite anions.

A further object of the invention is to provide a method of the character noted that may be readily carried out by a laboratory technician and that involves merely the preparation of a test solution from previously prepared stock solutions and an appropriate aliquot of the sample solution followed by simple manipulation of the test solution to insure a predetermined molybdenum-blue reaction therein, and the subsequent measurement of the light transmission characteristic of the blue coloration of the test solution employing a standard spectrophotometer.

Further features of the invention pertain to the particular arrangement of the steps of the method, whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawing, in which the single figure comprises a calibration curve illustrating the relationship between the light transmission characteristics and the hypophosphite anion concentrations of standard test solutions involving the molybdenum-blue reaction.

The method of the present invention is predicated upon the blue coloration resulting from the reaction of hypophosphorous acid and hypophosphite with molybdic acid, the light transmission characteristic of the blue coloration being employed as an index of the hypophosphite anion concentration or content of the test solution when the reaction mentioned is controlled to go to a predetermined state of completion under certain standard conditions. In carrying out the method, the molybdenum-blue reaction is carried to the predetermined state of completion in the test solution under certain standard conditions, and then the light transmission characteristic of the blue coloration thereof is measured employing a standard spectrophotometer, or the like, to establish the index mentioned. This index is then matched against a previously prepared calibration curve produced from the spectrophotometer employing different standard solutions of known hypophosphite anion concentrations or contents in which the molybdenum-blue reaction has been carried to the predetermined state of completion under the certain standard conditions, thereby to obtain the hypophosphite anion concentration or content of the test solution.

Specifically, it has been discovered that the reduction of molybdate anion by hypophosphite anion in a weak acid solution, once triggered by a soluble sulfite, will proceed at a rate that is a function of the hypophosphite anion concentration, of the pH, of the temperature, and of the light intensity; and that, at a suitable pH, the relationship between reaction rate and hypophosphite anion concentration follows a straight-line until the reaction is about half completed, provided the molybdate anion concentration is between 0.1% and 0.3%, and the hypophosphite anion concentration is not higher than about 20 parts per 1,000,000, by weight. It has also been discovered that phosphite anions and organic acid radicals do not interfere with the reaction unless the concentration thereof is over about twenty times that of the hypophosphite anion concentration. The reaction rate of molybdate anions and hypophosphite anions under the above conditions is very slow at room temperature, but increases rapidly as the temperature is elevated; whereby in the method, the reaction rate is accelerated by heating the test solution for a fixed time interval, at a fixed temperature, and at a fixed pH, with critical limits of concentrations of the reactants so as to obtain a predetermined state of completion of the molybdenum-blue reaction in order to obtain a blue color intensity bearing a straight-line relationship with respect to the hypophosphite anion concentration.

In accordance with the method of the present invention, a boric acid stock solution, a sodium sulfite stock solution, and a molybdic acid stock solution are first prepared. The boric acid stock solution essentially comprises boric acid dissolved in distilled water, approximately 4.95 gms. of boric acid per 100 cc. of water; and the sodium sulfite stock solution essentially comprises sodium sulfite dissolved in distilled water, approximately 5.00 gms. of sodium sulfite per 250 cc. of water. In preparing the molybdic acid stock solution 20.0000 ± 0.0009 gms. of molybdic acid is weighed out and dissolved in 25 cc. of 20% sodium hydroxide by gentle boiling; after complete dissolution of the molybdic acid, the solution is cooled and transferred quantitatively to a 200 cc. volumetric flask and diluted to 200 cc. with distilled water. This molybdic acid stock solution is filtered, if necessary, and stored in a stoppered bottle.

In carrying out the method, a molybdic acid-sulfuric acid solution is next prepared by placing 50 cc. of the molybdic acid stock solution in 12½ cc. of concentrated sulfuric acid and diluting to 100 cc. of distilled water. Then 5 cc. of the boric acid stock solution is measured

with a graduate and placed in a flask; 5 cc. of the sodium sulfite stock solution is measured with a burette and placed in the flask mentioned; and 5 cc. of the prepared molybdic acid-sulfuric acid solution is measured with a pipette or burette and placed in the flask mentioned. The sample solution, the hypophosphite anion concentration or content of which is to be determined, is first diluted, employing distilled water, to about 5 to 20 parts per 1000 parts of the dilute solution depending upon the initial hypophosphite concentration thereof. An appropriate aliquot of this dilute sample solution is then placed in the flask mentioned and the volume thereof is adjusted, employing distilled water, to produce 100 cc. of the test solution.

Recapitulating, this test solution essentially comprises the measured quantities of the boric acid stock solution, the sodium sulfite stock solution and the prepared molybdic acid-sulfuric acid solution, as well as the aliquot of the sample solution, the aliquot being appropriate to bring the hypophosphite anion concentration or content in the test solution down into the predetermined range 1 to 7 parts of hypophosphite per 1,000,000 parts of the test solution, which is the optimum range for accurate colorimetric determination. More specifically, the test solution comprises approximately 0.2 gm. of molybdic acid/100 c., and at least 0.1 gm. of sodium sulfite/100 cc.

The test solution is then placed in a hot water bath or other thermostatically controlled device, for 30 mins., using a stop watch for the timing thereof, the temperature thereof being maintained at 50°±1° C., in order positively to insure a predetermined state (not beyond 50%) of completion of a molybdenum-blue reaction therein. In passing, it is noted that to obtain the predetermined state of completion of the molybdenum-blue reaction, a somewhat higher temperature may be used during a shorter time interval, or a somewhat lower temperature may be used during a longer time interval, but as a practical matter, the conditions mentioned are quite satisfactory and easy to maintain in the laboratory. However, in this analysis, there must be employed the temperature and the time interval that were established and employed in a prior calibration, as described hereinafter. O course, the molybdenum-blue reaction which occurs in the test solution produces a blue coloration thereof that has an intensity that is directly proportional to the hypophosphite anion concentration or content in the test solution.

A portion of the test solution is then transferred to the cell of a standard spectrophotometer, colorimeter, etc., and the light transmission thereof is measured. Specifically, a Fisher "Electrophotometer" was employed utilizing a cell having a width of one centimeter and an approximately monochromatic light source obtained by means of a red filter, No. 650A in the Fisher Catalog. When the aliquot of the sample solution is appropriate to bring the hypophosphite anion concentration or content of the test solution down into the predetermined range 1 to 7 parts of hypophosphite per 1,000,000 parts of the test solution and the molybdenum-blue reaction is carried to the predetermined state of completion, in the manner described, the Fisher "Electrophotometer" employing the cell and the filter mentioned should produce a reading indicating the light transmission characteristic of the test sample, the reading normally falling between about $2.3\times10^{-2\%}$ and $8.5\times10^{-2\%}$; which range of light transmission characteristic corresponds to that of test solutions containing the hypophosphite anion concentrations or contents in the predetermined range mentioned.

Thus the reading of the Fisher "Electrophotometer" comprises an index of the hypophosphite anion concentration or content of the test solution; and this index may be translated into terms of hypophosphite content in parts per million of the test solution by applying the index to a previously prepared calibration curve of the general character of that illustrated in the single figure of the drawing. From this calibration curve, the hypophosphite anion concentration or content of the test solution is determined, whereby the hypophosphite anion concentration or content of the sample solution may be readily calculated in view of the known dilution of the sample solution and the amount thereof employed in the preparation of the aliquot thereof involved in the test solution.

In preparing the calibration curve illustrated in the drawing, a plurality of standard test solutions containing known hypophosphite anion concentrations or contents were prepared over the predetermined range mentioned. These standard test solutions were then manipulated, in the manner described above, in order to insure the predetermined state of completion of the molybdenum-blue reactions therein; and ultimately these standard test solutions were transferred to the Fisher "Electrophotometer" employing the cell and filter mentioned so that readings were obtained of the light transmission characteristics thereof. These readings of the light transmission characteristics of the standard test solutions taken from the Fisher "Electrophotometer" were plotted against the actual and known hypophosphite anion concentrations or contents of the respective standard test solutions in order to obtain the straight-line calibration curve illustrated.

It has been discovered that the accuracy of the present method is greatly enhanced by employing the relatively narrow predetermined range of the hypophosphite anion concentration or content in the test solution and by employing the small quantities of the boric acid stock solution and the sodium sulfite stock solution. The small quantity of boric acid in the test solution constitutes a buffer maintaining the pH thereof at about 4.5 and masking or complexing any interfering ions. The small quantity of sodium sulfite in the test solution triggers the molybdenum-blue reaction and intensifies the blue coloration thereof so that the transmission characteristic thereof is substantially completely dependent upon the hypophosphite anion concentration or content of the test solution. In the molybdenum-blue reaction, the molybdate anion is reduced to a blue colloidal compound of lower valance, and possibly of the approximate formula: MoO_2, $4MoO_3$, xH_2O. In any case, the blue coloration in the test solution is readily reproducible when the molybdenum-blue reaction is controlled to go to the predetermined state of completion under the conditions described, whereby the method comprises a satisfactory and ready scheme for the determination of the hypophosphite anion concentration or content in the test solution. It is important that the molybdenum-blue reaction in the test solution is not carried toward completion beyond about 50% in order to preserve the straight-line relationship between the transmission characteristic of the blue coloration of the test solution and the hypophosphite anion concentration or content thereof. Also it is important to note that the test solution may contain up to about 400 parts of phosphite anion per 1,000,000 parts of test solution without any interference with the blue coloration produced by the molybdenum-blue reaction. The mechanism involved in the prevention of interference of the phosphite anions is unknown, but in any case, the phenomenon is remarkable in that it has always been assumed that the molybdenum-blue reaction was not useful for even qualitative analysis in the presence of phosphite anions. In passing, it is noted that in the event the phosphite anion concentration or content of the test solution substantially exceeds 400 parts per 1,000,000 parts of the test solution that there is interference with the molybdenum-blue coloration, a greenish-blue coloration being produced in the test solution instead of the true molybdenum-blue coloration, previously described.

In connection with the present method, it is noted that the approximate composition of a sample solution with respect to the hypophosphite content thereof is usually known; whereby the taking of the proper aliquot therefrom to obtain in the test solution the hypophosphite anion content in the predetermined range 1 to 7 parts per 1,000,000 parts of the test solution, presents no problem. However, even when the approximate composition of the sample solution with respect to the hypophosphite anion content thereof is unknown, no difficult problem is involved, as then a first aliquot is taken based upon an assumed hypophosphite anion content in the sample solution; and a first analysis is made in accordance with the present method, as described above. In this case, the blue coloration of the test solution will prove to be below or within or above the range of the spectrophotometer, depending upon the accuracy of the assumption mentioned; whereupon a second analysis is made, if necessary, employing a second and adjusted aliquot of the sample solution, dependent upon the results of the first analysis. In this manner, it is obvious that the approximate composition of the sample solution with respect to the hypophosphite anion content thereof may be quickly established, so that a final and accurate analysis may then be carried out in accordance with the present method.

As previously noted, the method of the present invention is particularly useful in determining the hypophosphite concentration or content of a chemical nickel plating bath of the character of that employed in the continuous process disclosed in the copending application of Talmey and Crehan, previously mentioned, which process employs a bath of the nickel cation-hypophosphite anion type and preferably is of the composition of that disclosed in the copending application of Gregoire Gutzeit and Ernest J. Ramirez, Serial No. 204,424, filed January 4, 1951, now Patent No. 2,658,842, granted November 10, 1953. The bath disclosed in the Gutzeit and Ramirez application essentially comprises nickel cations that may be derived from commercial nickel chloride, hypophosphite anions that may be derived from sodium hypophosphite, and an exaltant in the form of a simple short chain saturated aliphatic dicarboxylic acid. In this bath, the ratio between nickel cations and hypophosphite anions, expressed in molar concentrations, is within the range 0.25 to 1.60; the absolute concentration of hypophosphite anions, expressed in mole/liter, is within the range 0.15 to 1.20; and the absolute concentration of the exaltant is approximately two carboxyl groups for every nickel cation that can be deposited, for instance, in the case of sodium succinate, at least 0.05 mole/liter of succinate anion. The initial pH of the bath is within the approximate range 4.3 to 6.8, and the temperature of the bath is maintained slightly below the boiling point thereof, about 99° C., at atmospheric pressure, in carrying out the nickel plating process.

For the purpose of verifying the usefulness of the present method in determining the hypophosphite anion concentration or content of a chemical nickel plating bath of the character of that described above, a plurality of standard sample baths were produced, each of the standard sample baths or solutions having a volume of 100 cc., and the standard sample solutions having variable known hypophosphite anion concentrations or contents, as explained more fully below. Specifically, each of the standard sample baths comprised nickel cations derived from an aqueous commercial nickel chloride stock solution containing 9.65% nickel, succinate anions derived from an aqueous sodium succinate stock solution containing 32.4 gms. of sodium succinate/liter, lactic acid derived from an aqueous lactic acid stock solution containing 85% lactic acid, hypophosphite anions derived from an aqueous sodium hydrophospite stock solution containing 62.3 gms. of sodium hypophosphite/liter, and water. In making up each of the standard sample solutions 5.5 cc. of the nickel chloride stock solution, 25 cc. of the sodium succinate stock solution, 3 cc. of the lactic acid stock solution, variable aliquots of the sodium hypophosphite stock solution, and distilled water were employed, whereby each of the standard sample solutions was diluted to a volume of 100 cc. These standard stock solutions contained variable hypophosphite anion concentrations or contents as determined by the aliquots of the sodium hypophosphite stock solution that were used. In view of the aliquots of the sodium hypophosphite stock solution that were employed, the hypophosphite anion concentrations or contents of the standard sample solutions were readily calculated and were accordingly known. The standard sample solutions were then employed in the production of test solutions in accordance with the method of the present invention, above described, appropriate aliquots being taken from the standard sample solutions and employed in the production of the corresponding test solutions. Finally, the test solutions thus produced were manipulated in the manner previously described in order to bring about the predetermined state of completion of the molybdenum-blue reaction therein, and were then transferred to the Fisher "Electrophotometer" and readings taken therefrom to provide the indices of the hypophosphite anion concentrations or contents thereof. Finally, the hypophosphite anion concentrations or contents of the test solutions thus determined experimentally were employed in calculating the initial hypophosphite anion concentrations or contents of the standard sample solutions and the calculated hypophosphite anion concentrations or contents thus produced were compared with the known hypophosphite anion concentrations or contents of the standard sample solutions, whereby a satisfactory degree of accuracy was obtained as indicated by the tables below:

Table No. 1

Standard Sample Solution	cc. of Sodium Hypophosphite Stock Solution Employed	Known Sodium Hypophosphite content of Std. Solution, Gms/liter
1	25.0	15.58
2	29.5	18.38
3	32.0	19.93
4	38.0	23.67
5	41.5	25.85
6	44.5	27.72
7	47.0	29.28
8	48.5	30.22
9	50.00	31.15

Table No. 2

Standard Test Solution Derived from Corresponding Standard Sample Solution	Experimental Percent Transmission×1,000 obtained from the Fisher "Electrophotometer"	Hypophosphite Anion Concentration in Std. Test Solution, Parts per 1,000,000	Experimentally Determined (Calculated) Sodium Hypophosphite Concentration in St. Sample Solution, Gms./Liter
1	43.8	4.02	16.08
2	36.9	4.80	19.20
3	68.7	1.98	19.80
4	62.4	2.42	24.20
5	60.5	2.55	25.50
6	57.0	2.83	28.30
7	55.4	2.96	29.60
8	53.4	3.12	31.20
9	52.2	3.20	32.00

By comparison of the known sodium hypophosphite concentration of the standard sample solutions derived from Table No. 1, appearing above, with the experimentally determined sodium hypophosphite concentrations of the standard sample solutions derived from Table No. 2, appearing above, it will be apparent that the percent errors in the respective tests were only: +3.21, +4.46, −0.65, +2.24, −1.35, +2.09, +1.09, +3.23 and +2.73; whereby it is obvious that the method of the present invention is entirely satisfactory for commercial purposes.

In view of the foregoing, it is apparent that there has been provided an improved colorimetric method of determining the hypophosphite anion concentration or content of sample solutions, employing an improved test solution usable in conjunction therewith, which may be carried out quickly in a simple and ready manner permitting accurate control of industrial processes utilizing reagents containing hypophosphites.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is: :

1. The method of determining the hypophosphite content of a sample solution comprising producing an aqueous acid test solution consisting essentially of water, molybdic acid, a sulfite, a buffer, and an aliquot of said sample solution appropriate to bring the hypophosphite content of said test solution down into a predetermined range of approximately 1 to 7 parts of hypophosphite per 1,000,000 parts of said test solution by weight; heating said test solution at a temperature of about 50° C. for a time interval of about 30 minutes to obtain a molybdenum-blue reaction therein; and measuring the light transmission characteristic of the blue coloration of said test solution to obtain an index of the hypophosphite content thereof within said predetermined range.

2. The method set forth in claim 1; wherein said buffer is boric acid.

3. The method set forth in claim 1; wherein the pH of said test solution is about 4.5.

4. The method set forth in claim 1; wherein said test solution contains about 0.2 gm. of molybdic acid per 100 cc., and at least 0.1 gm. of sodium sulfite per 100 cc.

5. The method set forth in claim 1; and further comprising comparing said index to a previously prepared calibration curve of light transmission characteristics of

similar solutions of known hypophosphite contents within said predetermined range in order to derive a value of the actual hypophosphite content of said test solution.

6. The method of determining the hypophosphite content of a sample solution comprising producing an aqueous acid test solution consisting essentially of water, molybdic acid, sulfuric acid, a sulfite, boric acid, and an aliquot of said sample solution appropriate to bring the hypophosphite content of said test solution down into a predetermined range of approximately 1 to 7 parts of hypophosphite per 1,000,000 parts of said test solution by weight; heating said test solution at a temperature of about 50° C. for a time interval of about 30 minutes to obtain a molybdenum-blue reaction therein; and measuring the light transmission characteristic of the blue coloration of said test solution to obtain an index of the hypophosphite content thereof within said predetermined range.

7. The method of determining the hypophosphite content of a sample solution comprising producing a test solution; wherein 100 cc. of said test solution essentially comprises approximately 5 cc. of a boric acid stock solution, approximately 5 cc. of a sodium sulfite stock solution, approximately 5 cc. of a molybdic acid-sulfuric acid solution, an aliquot of said sample solution appropriate to bring the hypophosphite content of said test solution down into a predetermined range of approximately 1 to 7 parts of hypophosphite per 1,000,000 parts of said test solution by weight, and the balance water; wherein said boric acid stock solution contains about 5 gms. of boric acid per 100 cc. of water, said sodium sulfite stock solution contains about 5 gms. of sodium sulfite per 250 cc. of water, said molybdic acid-sulfuric acid solution contains in approximately 100 cc. thereof about 50 cc. of a molybdic acid stock solution and about 12½ cc. of concentrated sulfuric acid and the balance water, and said molybdic acid stock solution contains in approximately 200 cc. thereof about 20 gms. of molybdic acid and about 25 cc. of 20% sodium hydroxide and the balance water; heating said test solution at a temperature of about 50° C. for a time interval of about 30 minutes to obtain a molybdenum-blue reaction therein; and measuring the light transmission characteristic of the blue coloration of said test solution to obtain an index of the hypophosphite content thereof within said predetermined range.

8. The method of determining the hypophosphite content of a sample solution also containing phosphite comprising producing an aqueous acid test solution consisting essentially of water, molybdic acid, a sulfite, a buffer, and an aliquot of said sample solution appropriate to bring the hypophosphite content of said test solution down into a predetermined range of approximately 1 to 7 parts of hypophosphite per 1,000,000 parts of said test solution by weight and to bring the phosphite content of said test solution down into a range below 400 parts of phosphite per 1,000,000 parts of said test solution by weight; heating said test solution at a temperature of about 50° C. for a time interval of about 30 minutes to obtain a molybdenum-blue reaction therein; and measuring the light transmission characteristic of the blue coloration of said test solution to obtain an index of the hypophosphite content therein within said predetermined range.

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