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COMPOSITION FOR AND METHOD OF DETERMINING CHROMATE CONCENTRATIONS

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16 Claims. (Cl. 23—230)

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The present invention relates to a composition for and method of determining chromate concentrations and more particularly to a composition for and method of determining the concentration of a water soluble chromate compound in aqueous solutions thereof, such as are used in the cooling systems of internal combustion engines to inhibit the formation of rust on the walls of such cooling systems.

In the cooling of power plants such as internal combustion engines, particularly when in use in large installations, such as stationary power plants or diesel locomotives, it is customary to add a rust inhibitor to the cooling water to prevent oxidation of those parts of the engine in contact with the cooling water. One such inhibitor in common use is a water soluble chromate, such as an alkali metal chromate. It has been found that a mixture of equal parts by weight of an alkali metal dichromate and an alkali metal carbonate is an effective rust inhibitor when employed in amounts by weight equivalent to 500 parts or more of sodium chromate per million parts of water. The chromate solution must be maintained at a concentration above a minimum of around 500 parts per million in order that the rust inhibiting properties of the mixture may be fully realized. If the inhibitor concentration should fall substantially below that minimum, serious damage from rust may result, requiring removal of the engine from service and repair of replacement of the rusted parts of the engine.

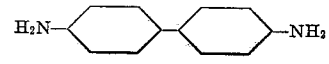
No simple and rapid method of determining the concentration of the chromate present in the cooling water has been heretofore provided. The standard method of quantitatively determining chromate concentration, such as by oxidizing the chromate to dichromate, adding an excess of a standard ferrous solution and titrating the excess ferrous ion against a standard solution of potassium bichromate, is useless in the hands of an unskilled mechanic or maintenance engineer. Further, it is impossible to employ such conventional methods where it is necessary to test the cooling water of a diesel powered locomotive while in motion, and where freshly prepared standard solutions of the reagents are not available.

The method herein provided makes possible the rapid determination of the inhibitor concentration by an operator while the power plant is in operation. The method is quick and simple and an accurate determination may be made by persons unskilled in the art of analytical chemistry.

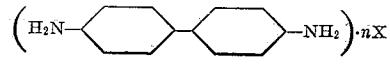
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It is unnecessary to provide special solutions, such as a standard ferrous or potassium bichromate solution.

The analytical composition of the present invention comprises a bibulous material impregnated with a solution of benzidine or an acid derivative of benzidine, the solution being sufficiently acid to convert chromate ions to dichromate ions. Benzidine is p,p' bianiline or more commonly diamino diphenyl (4-4') having the structural formula:



We have found that benzidine and acid derivatives of benzidine, such as benzidine hydrochloride (4,4' diamino diphenyl dihydrochloride) or benzidine acetate (4,4' diamino diphenyl diacetate), may be employed. Benzidine sulfate may be employed, but is inferior to the reagents above listed due to its relative insolubility in water and alcohol. The acid derivatives of benzidine suitable for use in the composition of the present invention may be generally indicated by the following structural formula:



where X is a halogen or carboxylic acid and n is an integer.

Benzidine is slightly soluble in water, but is soluble in alcohol or alcohol and water mixtures. The halogen and carboxyl acid derivatives of benzidine are water soluble and alcohol soluble. For use in the present invention, the solution contains an amount of acid sufficient to reduce the pH of the solution to a value of less than 7 in order to convert the chromate ions of the solution undergoing test to dichromate ions. This reaction in the presence of hydronium ion occurs as follows:

$$2(CrO_4) = +2(H_3O) + \rightarrow (Cr_2O_7) = +3H_2O$$

The hydronium ion necessary for the conversion may be furnished by the acid benzidine derivative or, preferably, by the addition of acid to the solution. It is further preferred that the acid employed to acidify the solution be a crystalline organic acid, for reasons to be hereinafter explained.

An aqueous or alcoholic solution of benzidine or of the acid derivatives of benzidine is colorless. It has been found that in the presence of oxidizing agents, such as chromates, or dichromates, the color of the benzidine or benzidine deriva-

tive solution undergoes a change. The exact color of the solution in the presence of the oxidizing agent depends upon the concentration of the oxidizing agent present in the material being tested. We have also discovered that this color change will occur when a solution containing an oxidizing agent is contacted with a bibulous material, such as absorbent paper, which has been impregnated with an acidified aqueous or alcoholic benzidine or benzidine acid derivative solution.

The color developed in the solution, or on the impregnated material, depends upon the chromate concentration of the material being tested. For example, we have found that as the chromate concentration is increased or decreased through a chromate concentration of approximately 1900 parts per million (3 lbs. of a mixture of equal parts by weight of sodium dichromate and sodium carbonate per 100 gal. of water) a definite, sharp color break occurs. This color change may be readily observed, and the change provides a simple and efficient method for determining the amount of chromate present in the material being tested.

The method of determining chromate concentrations as herein provided utilizes the change of color in the benzidine or benzidine derivative to determine quantitatively the amount of chromate present in the material undergoing tests. The colors developed upon contact between a paper impregnated with benzidine or a benzidine derivative, and a group of standard chromate solutions, each containing a known amount of chromate, are recorded and reproduced by any suitable method such as by a lithographic process. Since the color does not develop instantaneously upon placing a drop of the unknown chromate solution on the impregnated paper, it is best to permit 1½ to 2 minutes to elapse before judging the color, and this same procedure is followed in making up the standard color charts for comparison. To determine the chromate concentration in any given solution of unknown chromate concentration, a drop of the solution is merely placed on paper impregnated with a benzidine or benzidine derivative and the color developed after 1½ to 2 minutes of contact between the impregnated paper and the chromate solution is then compared with the colors on the standard color chart. Thus, the concentration of chromate in any solution of unknown concentration may be visually determined without the necessity of using any of the involved quantitative analysis procedures.

By the selection of a suitable weight ratio of a particular benzidine compound to the particular acid used in impregnating the bibulous paper, or other sheet material, and by the selection of a suitable concentration of the benzidine compound and acid in the impregnated paper, we can control the color change that is obtained when drops of standard chromate solutions of known concentrations are successively placed on the impregnated paper. With the preferred compositions hereinafter disclosed, the color change is from light blue through deeper blue, through golden to brownish gold. There is a definite, sharp color break from blue to completely golden at a chromate concentration of about 1900 parts of sodium chromate per million parts of water.

Since it happens that a concentration of about 1900 parts of sodium chromate per million parts of water is an optimum concentration for inhibiting rust formation, the definite, sharp color break at that concentration gives an excellent indication as to whether or not the particular solution of unknown chromate concentration that is being tested by the use of our color standards has that optimum concentration. If the solution undergoing test gives a color test that indicates a lower concentration of chromate than the optimum of about 1900 parts per million, sufficient sodium chromate or mixture of sodium chromate and sodium carbonate, is added until the optimum concentration is reached.

It is, therefore, an important object of the present invention to provide a composition for the determination of chromate concentrations which comprises a bibulous material impregnated with a solution of a compound selected from the group consisting of benzidine and acid derivatives of benzidine, the solution being sufficiently acid to convert chromate ions to dichromate ions.

It is a further important object of the present invention to provide a composition for the determination of chromate concentrations which comprise a relatively dry bibulous material that has been impregnated with a solution containing a compound having the structural formula:



where n is 0 or an integer and where X is a halogen or carboxylic acid, the solution being sufficiently acidic to convert chromate ions to dichromate ions.

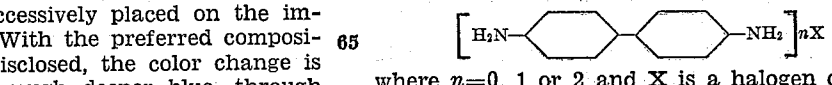
It is a further important object of the present invention to provide a method for determining chromate concentrations by placing a small portion of the chromate solution of unknown concentration on a test paper impregnated with a solution of benzidine or an acid derivative of benzidine, and comparing the color produced with a standard set of colors for known chromate concentrations.

It is a still further object of the present invention to provide a method for determining the chromate concentration of aqueous chromate solutions by placing a drop of the chromate solution on a test paper impregnated with a solution containing a compound having the structural formula:

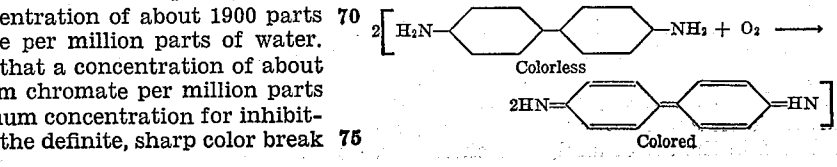


whene n is 0, or an integer and X is a halogen or carboxylic acid and the solution is sufficiently acidic to convert the chromate ions to dichromate ions, and comparing the color produced with a standard set of colors for known chromate concentrations.

As has been hereinbefore stated, the analytical composition of the present invention comprises a bibulous base material impregnated with a solution of benzidine or an acid derivative of benzidine. These benzidine compositions have the following general structural formulae:



where n=0, 1 or 2 and X is a halogen or carboxylic acid. The change of color in the benzidine solution is believed due to the following reaction:



Actually the change in the degree of color is believed to be due to the change in the proportionate amounts of the colored quinoid body and the colorless benzidine.

Rust and moisture corrosion of those parts of the engine in contact with the cooling water is greatly inhibited if sodium chromate is present in the cooling water at a concentration of 500 or more parts by weight per 1,000,000 parts by weight of the water. A concentration of about 1900 parts of sodium chromate per million, which is an optimum concentration, may be obtained by the addition of 3 pounds of a composition containing 50% by weight of sodium dichromate and 50% by weight of sodium carbonate to 100 gallons of cooling water. Such a solution has an alkalinity indicated by a pH value within the range of 8.5 to 10.5, which is accepted practice in railroad operation.

We have found that the color developed by benzidine or an acid derivative of benzidine in the presence of such a concentration of chromate is markedly different from that developed in the presence of higher or lower concentrations of chromate. In other words, at the critical point at which the concentration of chromate in the coolant is sufficient to prohibit rust and corrosion, a definite color break occurs and the color developed upon contact of a solution of such concentration with the bibulous material impregnated with a solution of benzidine or benzidine derivative is very noticeable.

In accordance with the method of the present invention, an absorbent or bibulous material, such as filter paper or common blotter paper, is impregnated with a solution containing benzidine or a benzidine acid derivative, such as benzidine di-hydrochloride or di-acetate. It is preferred that from 3 to 8 grams of benzidine or benzidine derivative be present per liter of solution. A sufficient amount of a crystalline organic acid, and preferably an hydroxy carboxylic acid such as tartaric acid or citric acid, is added to lower the pH of the solution to a value of less than 7.

Common non-crystalline acids that are available in aqueous solution, such as hydrochloric, sulfuric and the like, are not satisfactory because upon drying the blotting paper impregnated with such acids, either the acid is volatilized or the residual concentrated acid deteriorates the paper. Specifically, acetic acid has also been found unsuited for our purposes. We prefer to maintain the acid to benzidine or to benzidine derivative ratio at a value of approximately 20 to 1 to insure the presence of sufficient acid within the area of the blotter contacted by the drop of the unknown chromate solution to convert the chromate ions therein to dichromate ions upon contact with the impregnated material. Thus, the preferred impregnating solutions of the present invention may contain from 60 to 160 grams of crystalline acid per liter of solution. The acid added to regulate the pH of the solution must be an acid which will not form an insoluble complex with the benzidine or benzidine derivative.

If desired, starch, such as a corn or arrowroot starch, may be added to the composition to aid in the prevention of oxidation of the benzidine compound to the colored or quinoid form. We have found that the composition even when not containing starch is relatively resistant to such oxidation. However, the presence of the starch appears to inhibit the small amount of oxidation which might otherwise occur.

The solvent employed in preparing the analytical solution may be either an alcohol, such as ethyl alcohol, or water, or an aqueous alcohol mixture. The solvent employed depends upon the benzidine compound present. In the case of benzidine itself it is preferred that the solvent be alcohol, because of the insolubility of benzidine in water, while if benzidine di-hydrochloride or benzidine di-acetate is used it is preferred that the solvent be water.

A card formed of white absorbent paper or other bibulous sheet material is immersed in the above solution for 30 seconds, drained vertically for 30 seconds, and dried at a temperature between 60 and 70° C., the card being placed in horizontal position during the drying operation. The cards thus produced after being dried retain their original color and appearance for a substantial period of time to be considered stable for all practical purposes.

When prepared as above described, the solids content of the active ingredients in the impregnated card is such that the card is suitable for use in testing an alkaline chromate solution of a pH up to 10.5 and of a chromate concentration above more than a trace. In particular, the amount of acid within the area of spread of a drop of the unknown chromate solution, when placed upon the card is sufficient to acidify the drop and to convert the chromate ions present into dichromate ions for reaction with the benzidine compound present in the card to give a corresponding color indication.

The concentration of the chromate present in the cooling water is determined by merely placing a small portion of the coolant water upon the blotter, observing the color developed at the point of contact between the solution and the blotter if chromates are present in the solution, and comparing with a standard set of colors for known chromate concentrations.

In order that the operator, who desires to determine the concentration of any chromate solution, may have a ready visual reference with which to compare the colors produced upon contact between the chromate solution and the impregnated paper, it is preferred that the operator have before him a reference card carrying colors corresponding to those produced upon contact of standard solutions containing definite amounts of chromate with impregnated paper identical to that being employed by the operator. In order to provide such a reference or color index, the colors produced upon contact of standard solutions containing definite amounts, such as 0.125, 0.250, 0.50, 1.0, 2.0, 3.0 and 4.0 pounds of a mixture of equal parts by weight of sodium dichromate and sodium carbonate per 100 gallons of water, may be determined and such colors may then be reproduced, as by a suitable photolithographic process, to provide a permanent set of color standards.

Without limiting our invention to any particular procedure, the following examples in which parts by weight are given, will serve to illustrate our method in its preferred form.

Example

Aqueous solutions of a rust inhibitor consisting of 50% by weight of sodium dichromate and 50% by weight of sodium carbonate were prepared to yield the concentrations listed below.

Analytical compositions of the present invention were prepared by immersing separate ab-

sorbent paper blotters in each of the following compositions:

I.

1 gr. benzidine dihydrochloride
20 gr. citric acid
0.5 gr. corn starch
250 ml. water

II.

1 gr. benzidine di-acetate
20 gr. citric acid
0.5 gr. corn starch
250 ml. water

III.

1 gr. benzidine
20 gr. citric acid
0.5 gr. corn starch
250 ml. ethyl alcohol

The blotters were removed from contact with the solutions and drained vertically for 30 seconds, after which the blotters were dried at a temperature of between 60 and 70° C. with the blotters in a horizontal position.

A drop of each of the following standard chromate solutions of the concentrations indicated was contacted with the indicator paper impregnated with composition No. I, and the colors observed, as follows:

Chromate solution:

Pounds of inhibitor per 100 gal. water	Observed color
0.125	light blue
0.250	deeper than 1
0.50	deeper than 2
1.0	deeper than 3
2.0	golden with greenish-blue flecks
3.0	completely golden
4.0	golden brown
5.0	brownish gold

The same colors were observed upon contact of the standard chromate solutions of corresponding concentrations with blotters impregnated with each of the above listed compositions II and III and also with similar compositions containing 20 gr. of tartaric acid in place of citric acid.

In testing a chromate solution of unknown concentration, the same procedure is followed and the color obtained is matched against the standard set of colors. Adjustment of the concentration of the solution is then made, if necessary, and the adjusted solution again tested, if desired, as a check upon the correctness of the adjustment.

While we have described a preferred embodiment of our invention as applied to the testing of chromate solutions of unknown concentration, many variations are permissible. For instance, other standard sets of colors may be established by the use of other benzidine compounds and other crystalline organic acids, or by varying the concentrations thereof in the impregnated bibulous material. Using our preferred composition, however, gives a most satisfactory standard set of colors for the testing of alkaline chromate solutions such as are used in cooling systems for rust inhibition.

Also, while we have preferred to incorporate an acid in the impregnated bibulous material in a concentration sufficient to convert chromate ions into dichromate ions, when a drop of the unknown alkaline chromate solution is placed on the impregnated bibulous material, it would be possible to reduce the acid concentration in the impregnated material if the unknown chromate solution were less alkaline, or the acid might be omitted entirely from the impregnated solution if the unknown chromate solution were first acidified to convert the chromate ions into dichromate ions before making the color test.

It will, of course, be understood that various details of the process may be varied through a wide range without departing from the principles of this invention and it is, therefore, not the purpose to limit the patent granted hereon otherwise than necessitated by the scope of the appended claims.

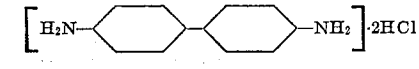
What we claim is:

1. A method for the determination of chromate concentration in an alkaline chromate solution of unknown concentration, which comprises impregnating a white bibulous sheet with an aqueous acid solution of from 60 to 160 grams per liter of solution of a crystalline organic acid selected from the group consisting of citric acid and tartaric acid and from 3 to 8 grams per liter of solution of a compound selected from the group consisting of benzidine, hydrochloric acid and acetic acid derivatives of benzidine, drying said impregnated sheet and placing a drop of said alkaline chromate solution on said dry sheet, the concentration of said acid and of said compound in said sheet being such that upon contact of said drop with said sheet a color will develop within the range from blue through golden to brownish gold depending upon the concentration of the chromate in said chromate solution.

2. A method for the determination of chromate concentration in an alkaline chromate solution of unknown concentration, which comprises impregnating a white bibulous sheet with an aqueous acid solution of citric acid and of a compound selected from the group consisting of benzidine and hydrochloric acid and acetic acid derivatives of benzidine, drying said impregnated sheet and placing a drop of said alkaline chromate solution on said dry sheet, the concentration of said acid and of said compound in said sheet being such that upon contact of said drop with said sheet a color will develop within the range from blue through golden to brownish gold depending upon the concentration of the chromate in said chromate solution.

3. A method for the determination of chromate concentration in an alkaline chromate solution of unknown concentration, which comprises impregnating a white bibulous sheet with an aqueous acid solution of tartaric acid and of a compound selected from the group consisting of benzidine and hydrochloric acid and acetic acid derivatives of benzidine, drying said impregnated sheet and placing a drop of said alkaline chromate solution on said dry sheet, the concentration of said acid and of said compound in said sheet being such that upon contact of said drop with said sheet a color will develop within the range from blue through golden to brownish gold depending upon the concentration of the chromate in said chromate solution.

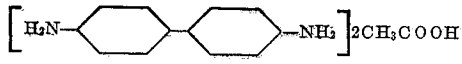
4. A method for the quantitative determination of the chromate concentration of an alkaline aqueous chromate solution which comprises providing a bibulous surface impregnated with an aqueous solution of a compound having the structural formula



and a quantity of citric acid sufficient to convert chromate ions in said chromate solution to

dichromate ions, placing a drop of said chromate solution of unknown concentration on said impregnated bibulous surface, and providing a standard set of colors produced by known chromate concentrations for comparison with the color produced by said solution of unknown concentration upon contact with said impregnated surface.

5. A method for the quantitative determination of the chromate concentration of an alkaline aqueous chromate solution which comprises providing a bibulous surface impregnated with an aqueous solution of a compound having the structural formula



and a quantity of citric acid sufficient to convert chromate ions in said chromate solution to dichromate ions, placing a drop of said chromate solution of unknown concentration on said impregnated bibulous surface, and providing a standard set of colors produced by known chromate concentrations for comparison with the color produced by said solution of unknown concentration upon contact with said impregnated surface.

6. A method for the determination of chromate concentrations of alkaline aqueous chromate solutions which comprises providing a solution of a compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate and citric acid, said constituents being present in the ratio of 1 part by weight of the aromatic amine per 20 parts by weight of the acid, placing a drop of said chromate solution of unknown concentration on said impregnated bibulous surface, and providing a standard set of colors produced by known chromate concentrations for comparison with the color produced by said solution of unknown concentration upon contact with said impregnated surface.

7. A method for the determination of chromate concentrations of an alkaline aqueous chromate solution which comprises providing a white bibu'ous material impregnated with a solution comprising from 3 to 8 grams per liter of solution of a compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate, and from 60 to 160 grams per liter of solution of a crystalline organic acid selected from the group consisting of citric acid and tartaric acid, placing a drop of said chromate solution of unknown concentration on said impregnated bibulous surface, and providing a standard set of colors produced by known chromate concentrations for comparison with the color produced by said solution of unknown concentration upon contact with said impregnated surface.

8. A composition for use in a method of determining chromate concentration of alkaline aqueous chromate solutions of unknown concentration comprising a dry sheet of white bibu'ous material impregnated with an aqueous solution of benzidine di-hydrochloride and a sufficient amount of citric acid to convert chromate ions in the unknown solution to dichromate ions when a drop of said unknown solution is placed on said impregnated sheet.

9. A composition for use in a method of determining chromate concentration of an alkaline aqueous chromate solution of unknown concentration comprising a dry sheet of white bibulous material impregnated with an aromatic amine compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate and with citric acid, said constituents being present in the ratio of 1 part by weight of the aromatic amine compound per 20 parts by weight of the acid.

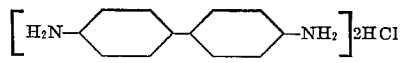
10. A composition for use in a method of determining chromate concentration of an alkaline aqueous chromate solution of unknown concentration comprising a dry sheet of white bibulous material impregnated with a compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate and with a sufficient concentration of tartaric acid to convert chromate ions in the unknown solution into dichromate ions when a drop of said unknown solution is placed on said impregnated sheet.

11. A method for the determination of chromate concentrations of an alkaline aqueous chromate solution which comprises providing a white bibulous material impregnated with a solution comprising a compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate, and a crystalline organic acid selected from the group consisting of citric acid and tartaric acid, placing a drop of said chromate solution of unknown concentration on said impregnated bibulous surface, and providing a standard set of colors produced by known chromate concentrations for comparison with the color produced by said solution of unknown concentration upon contact with said impregnated surface.

12. A composition for use in a method of determining chromate concentrations of an alkaline aqueous chromate solution of unknown concentration comprising a dry sheet of bibulous material impregnated with a solution of a compound selected from the group conssiting of benzidine, benzidine di-hydrochloride and benzidine di-acetate and an amount of crystalline organic acid selected from the group consisting of citric acid and tartaric acid sufficient to convert chromate ions in the unknown solutions to dichromate ions when a drop of said unknown solution is placed on said impregnated sheet, said crystalline organic acid and said compound being present in a ratio of approximately 20 to 1.

13. A composition for use in a method of determining chromate concentrations of an alkaline aqueous chromate solution of unknown concentration comprising a dry sheet of bibulous material impregnated with a solution of from 3 to 8 grams per liter of solution of a compound selected from the group consisting of benzidine, benzidine di-hydrochloride, and benzidine di-acetate, and from 60 to 160 grams per liter of solution of a crystalline organic acid selected from the group consisting of citric acid and tartaric acid.

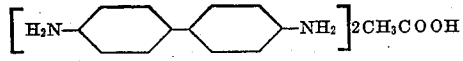
14. A method for the quantitative determination of the chromate concentration of an alkaline aqueous chromate solution which comprises impregnating a bibulous sheet with an alcoholic solution of a compound having the structural formula:



and a quantity of a crystalline organic acid selected from the grup consisting of citric acid and tartaric acid sufficient to convert chromate ion into chromate solution to dichromate ions,

drying said impregnated sheet, and placing a drop of said chromate solution of unknown concentration on said impregnated bibulous sheet, whereby the color developed on said sheet may be compared with a standard set of colors produced by known chromate concentration.

15. A method for the quantitative determination of the chromate concentration of an alkaline aqueous chromate solution which comprises impregnating a bibulous sheet with an alcoholic solution of a compound having the structural formula:



and a quantity of a crystalline organic acid selected from the group consisting of citric acid and tartaric acid sufficient to convert chromate ion into chromate solution to dichromate ions, drying said impregnated sheet, and placing a drop of said chromate solution of unknown concentration on said impregnated bibulous sheet, whereby the color developed on said sheet may be compared with a standard set of colors produced by known chromate concentration.

16. A composition for use in a method of determining chromate concentration of an alkaline aqueous chromate solution of unknown concentration comprising a dry sheet of dry bibulous material impregnated with an aqueous solution of a compound selected from the group consisting of benzidine and hydrochloric and acetic acid derivatives of benzidine, and a sufficient amount of a crystalline organic acid selected from the group consisting of citric acid and tartaric acid to convert chromate ions in the unknown solution to dichromate ions when a drop of said unknown solution is placed on said impregnated sheet.

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MELVIN A. HANSON.

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