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TESTING FOR QUATERNARY AMMONIUM COMPOUNDS

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This invention relates to testing for quaternary ammonium compounds and, more particularly, to a reagent solution for quantitatively differentiating between solutions containing small concentrations of quaternary ammonium compounds and to the test method employed.

Because of their bactericidal action, many quaternary ammonium compounds have been widely adopted in rinses and formulated detergent preparations for sanitizing purposes. To insure sanitary cleanliness, it is necessary that the quaternary compound be present in amounts exceeding certain minimum use concentrations which are frequently prescribed by health authorities. A large number of test procedures, ranging widely in complication and accuracy of results, have been developed in order to measure the concentration of quaternary compound in the use solutions. Many of these tests employ bromphenol blue (tetrabromphenolsulfonthalein), an indicator dye, which forms a complex with the quaternary ammonium compounds, and determines the concentration of a quaternary compound by colorimetric titration. In the procedures now known, the water insoluble dye-quaternary complex is extracted into an organic solvent in the course of titration or prior to making the colorimetric determination based on color intensity, thus making it necessary to work with a two-phase solvent mixture. Consequently, these prior art procedures are somewhat complex to the layman and require considerable time as well as the skill of a trained technician to be properly performed. The accuracy of these tests is, in many cases, detrimentally affected by hard water, milk, beer, and even synthetic detergents and soaps.

An object of this invention, therefore, is to provide a single aqueous reagent solution that will distinguish minimum use concentrations of quaternary ammonium compounds from marginal or improperly dilute solutions of these compounds.

Another object of this invention is to provide a reagent solution which will give accurate indications as to the concentration of the quaternary ammonium compounds, both in alkali and neutral solutions and in the presence of hard water, milk, and other foreign matter normally encountered in use solutions.

Still another object of this invention is to provide a method of testing use solutions of quaternary ammonium compounds in order to distinguish minimum use concentrations from improperly dilute solutions, which comprises merely intermixing a certain reagent with the use solution and making an immediate colorimetric determination in a single phase solution, without any intervening steps such as extraction by organic solvents.

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Other objects and advantages of the present invention will become apparent from the following detailed description thereof.

It has been found that an accurate, simple test for quaternary ammonium compounds may be made by adding to a known amount of use solution containing a quaternary ammonium compound a prescribed amount of a reagent solution consisting essentially of a buffered acetic acid, water solution of bromphenol blue.

The amount of bromphenol blue in the test reagent solution is so regulated that, when the test solution is added to a prescribed quantity of the use solution containing the quaternary ammonium compound, all of the bromphenol blue dye reacts with the quaternary ammonium compound to form a blue-violet complex if the quaternary compound is present in an amount equal to or greater than the prescribed minimum use concentration. When the quaternary compound is present in approximately half the minimum use concentration, a mixture of the blue-violet complex plus the yellow color of the excess dye in acid solution produces a green colored solution. In use solutions wherein the quaternary compound falls far below the minimum use concentration, very little, if any, dye-quaternary complex is formed and the solution remains yellow. It is essential to keep in mind, however, that all of these determinations of the color of the solution must be made by transmitted light in order to avoid the reddish tints obtained when viewing these solutions by reflected light. Also, the color of these solutions varies continuously as the quaternary present varies, so that intermediate shades of blue green, green blue, yellow green and greenish yellow will be seen at concentrations intermediate between 200 and 100, and 100 and 0 p. p. m. of quaternary.

The following reagent solution is illustrative of the present invention:

	Percent by weight
Bromphenol blue	0.08
Sodium acetate C. P. ($NaC_2H_3O_2.3H_2O$)	12.50
Glacial acetic acid	62.50
Distilled water	24.92

This solution is quite easily prepared by dissolving the bromphenol blue in the glacial acetic acid and water mixture, and then adding the acetate salt. In preparing large volumes, the solution of the dye may be hastened by first dis-

solving it in a minimum amount of 95% ethyl alcohol.

The amount of bromphenol blue employed will be determined by the end point desired, that is, the prescribed quaternary minimum use concentration. Where the permissible minimum use concentration is quite high, larger amounts of bromphenol blue must be employed, and for a lower permissible minimum use concentration of the quaternary compound, smaller amounts of bromphenol blue must be employed.

Since improperly dilute solutions are detected by the use of the yellow color of the bromphenol dye in acid solution, excess glacial acetic acid is added in order to insure the fact that the final test solution (reagent solution+use solution) has a pH of approximately 3.0. The importance of the hydrogen ion concentration in the final test solution will become apparent when it is considered that the dye employed is a pH indicator in that it is yellow below a pH of 3.6 and blue above this pH value. Since the instant test is dependent upon the blue or blue-violet color of the dye-quaternary complex in combination with the yellow color of the uncombined dye in acid solution, it is necessary to maintain the pH below 3.6. On the other hand, highly acid solutions appear to interfere with the formation of the dye-quaternary complex and thus prevent an accurate test of the amount of quaternary present. For example, a reagent solution intended to test the minimum use concentration of 200 p. p. m., was blue at a pH of 3.0, but turned green upon lowering the pH of the solution to 2.5. Consequently, it is necessary to maintain the pH of the final test solution at approximately 3.0 ± 0.25. The sodium acetate salt is a buffering agent which assists in maintaining the reagent solution within the relatively critical pH range. The addition of this buffering agent permits accurate testing of both neutral and slightly alkaline use solutions, as well as the testing of both hard and soft water use solutions.

It will be apparent from the above discussion that the reagent solution must be very critically balanced as regards its various components, and this has been found to be particularly true in regard to the ratio of the buffering salt to the acetic acid. Preferably this ratio is maintained at one part of buffering salt to five parts of acetic acid, although the amount of acetic acid may be increased until the solution contains one part buffering salt to seven parts acetic acid. Such variation in ratio may necessitate slight adjustment to the amount or composition of the reagent solution used.

In accordance with the method of the present invention, the bromphenol blue concentration in the reagent solution is so selected that at a use concentration of the prescribed minimum or greater, all of the dye will react with the quaternary compound to produce the blue-violet complex. Different quaternary compounds will require different amounts of reagent solutions, but the desired quantity may be readily determined by simple experimental procedure. At a minimum use concentration of 200 p. p. m., accurate tests were made of use solutions containing the quaternary ammonium compounds di-isobutylphenoxyethoxyethyldimethylbenzyl ammonium chloride and methyldodecylbenzyltrimethyl ammonium chloride, by adding 0.4 ml. of the reagent solution given above to 6.0 ml. of these use solutions. After adding the reagent solution to the use solution, the two are mixed by shaking

slightly and the color then observed by transmitted light. It is desirable to observe the color of the solution immediately, since this color may change slightly upon standing. If the minimum use concentration of at least 200 p. p. m. is present, the final test solution will be blue or blue-violet, since all of the dye is tied up in the dye-quaternary complex. If the concentration of quaternary ammonium compound is approximately 100 p. p. m., a green colored solution will result due to presence of both the blue dye-quaternary complex and the yellow uncombined dye. Yellow-colored solutions are obtained where 50 p. p. m. or less of the quaternary compound is present, since the yellow uncombined dye predominates.

From the above description, it is readily apparent that a test for quaternary ammonium compounds, particularly in sanitizing compositions, has been provided which is extremely simple in procedure and may be easily performed by nontechnical personnel. By the use of a single reagent solution, and without any organic solvents involved, it is possible to quickly determine whether or not the minimum use concentration of the quaternary ammonium compound is present in the use solution and, if not, approximately how far below minimum standards the use solution falls. It should also be noted that the reagent solution is quite stable as well as being economical to produce. The speed of the test herein described is such as to encourage its wide use in the field by health inspectors, sanitarians, dishwashers, bartenders and the like. Furthermore, the above described test may be employed on use solutions containing either hard or soft water, as well as the usual foreign inclusions normally found in dishwater and the like. The combination of simplicity, low cost, speed of testing and accuracy make this the first test for quaternary ammonium compounds that is practical for field testing rinses and formulated detergent preparations for use in the sanitizing field.

Variations and modifications of the present invention, as above set forth, will become apparent to those skilled in the art, and such modifications as fall within the scope of the hereinafter appended claims are deemed to form a part of this invention.

What is claimed is:

1. A method for determining when the concentration of a quaternary ammonium germicidal compound in an aqueous solution falls below a prescribed minimum level, which comprises preparing a reagent solution consisting essentially of bromphenol blue, sodium acetate, glacial acetic acid and distilled water, adding this reagent solution to a quaternary ammonium germicidal solution in an amount such that the bromphenol blue is present in a stoichiometric amount relative to the calculated prescribed minimum concentration of the quaternary ammonium compound, the ratio of sodium acetate, glacial acetic acid and water being regulated so that the resulting mixture of reagent solution and quaternary ammonium germicidal solution has a pH of 3.0 ± 0.25, mixing the two solutions, examining the resulting solution through transmitted light in order to determine from the color of the final solution if the concentration of the quaternary ammonium compound has fallen below the prescribed minimum concentration.

2. A method for determining when the concentration of a quaternary ammonium germicidal

compound in an aqueous solution falls below 200 p. p. m., which comprises preparing a reagent solution consisting essentially of about 0.08% bromphenol blue, about 12.50% sodium acetate, about 62.50% glacial acetic acid and about 24.92% distilled water, adding approximately 0.4 ml. of the reagent solution, to approximately 6.0 ml. of the quaternary ammonium germicidal solution, mixing the two solutions, examining the resulting solution through transmitted light in order to determine from the color of the final solution if the concentration of the quaternary ammonium compound has fallen below 200 p. p. m.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,721,809	Buchanan	July 23, 1929
2,178,550	Acree	Nov. 7, 1939
2,471,861	Cahn	May 31, 1949

OTHER REFERENCES

Colichmann: I. and E. Chem., Anal. ed., vol. 19 (1947), pages 430–1.