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F. J. CAHN

2,471,861

TESTING OF SOLUTIONS

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Fig. 1.

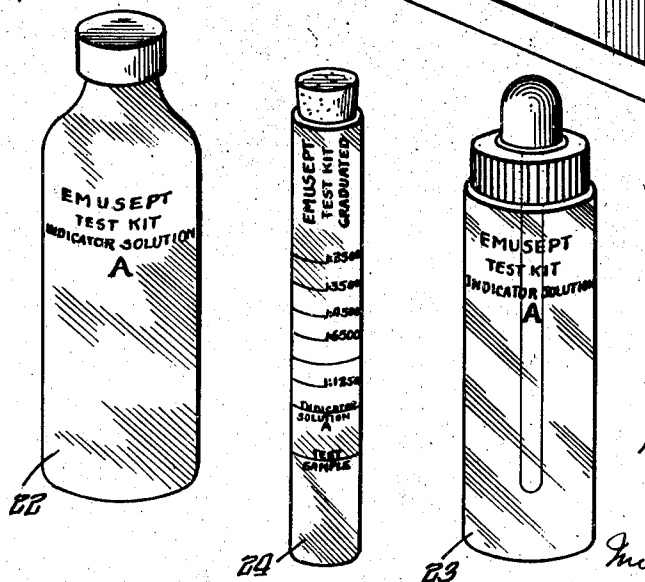
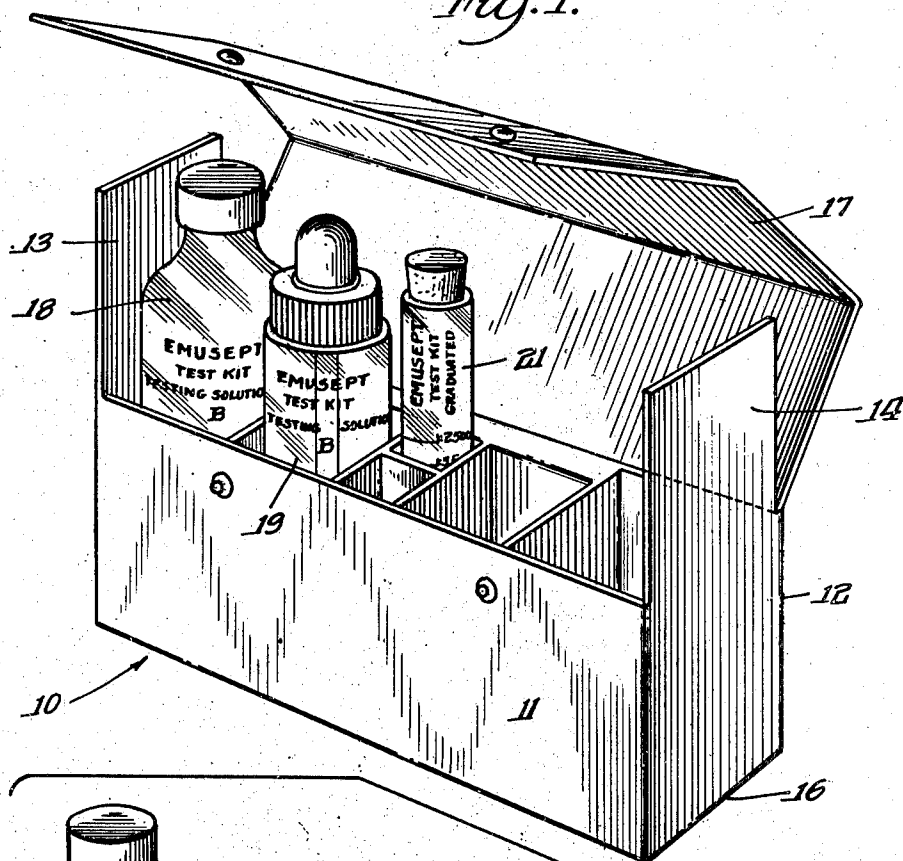


Fig. 2.

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UNITED STATES PATENT OFFICE

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TESTING OF SOLUTIONS

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7 Claims. (Cl. 23-230)

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My invention relates to the testing of aqueous solutions of either anionic compounds or cationic quaternary ammonium compounds to determine the concentration thereof, the invention having particular utility in connection with the testing of dilute solutions of certain types of cationic quaternary ammonium compounds as hereinafter described in detail.

Quaternary ammonium compounds containing a lipophile group, such as an aliphatic hydrocarbon chain of about 12 carbon atoms or more, are used in industry for a variety of purposes as, for example, germicides, bactericides, antiseptics, preservatives, detergents, ore flotation agents, emulsifying agents, textile treating agents, and the like. Such compounds are, in general, of high potency and it is common practice, therefore, to utilize them in dilutions of the order of 1 part to 1000 parts of water or in even materially greater dilutions. These low concentrations render it important, particularly for field testing and control work, to have available a test method which is accurate and rapid and which may be carried out with simple equipment.

It has heretofore been suggested to test or determine the concentration of quaternary ammonium compounds by a method which comprises forming a salt of the quaternary ammonium compound contained in the solution thereof to be tested with bromothymol or bromophenol blue in aqueous sodium carbonate solution, extracting the colored salt which is formed with ethylene dichloride, drying the non-aqueous layer with sodium sulfate, filtering, and measuring the intensity of color so extracted by means of a photoelectric colorimeter. The intensity of the color is determined by comparing with the color similarly produced in a solution containing a known amount of the same quaternary ammonium compound. This known method, while reasonably satisfactory from certain standpoints, has several objectionable aspects, particularly in regard to such factors as simplicity and rapidity as well as the cost and availability of the particular equipment required.

In accordance with my present invention, the determination of the concentration of a cationic quaternary ammonium compound in the form of a dilute aqueous solution thereof is measured by virtue of certain changes which take place by the addition thereto of an equivalent amount of an anionic compound. More specifically, I have found that, when a few drops of dichlorofluorescein indicator solution are added to a dilute colorless or substantially colorless solution of

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a cationic quaternary ammonium compound, the solution becomes colored pink to red in transmitted light, the exact tint depending upon the particular cationic quaternary ammonium compound employed. When this solution is titrated with a dilute solution of an anionic compound, the pink or reddish color disappears at or near the equivalence point. I have also found that this color change can be more easily observed and the equivalence point more sharply perceived by introducing a water-immiscible organic solvent into the system, particularly suitable solvents being chlorinated compounds illustrative examples of which are ethylene dichloride and chloroform. The organic solvents become colored when in equilibrium with the aqueous phase containing the free cationic quaternary ammonium compound and lose the color when the system becomes void of the free cationic quaternary ammonium compound after the addition of the equivalent amount of anionic compound to the system. The color changes are reversible, making back titration readily feasible.

In an illustrative example of the practice of the method of my present invention, 25 cc. of the solution of the cationic quaternary ammonium compound to be tested, the concentration of which solution is of the order of 0.001 M or less, are placed in a 50 cc. stoppered tube or cylinder, 5 cc. of chloroform and 3 drops of a 0.1% dichlorofluorescein alcohol solution are then added, and the mixture is shaken. The resulting chloroform-in-water emulsion becomes colored pink and, if the emulsion is allowed to separate, the upper aqueous layer and the lower chloroform layer appear pink in transmitted light. A standardized dilute aqueous solution of an anionic compound is then added gradually, in portions, with shaking after each addition, until the emulsion is only faintly colored. At this step, the chloroform layer settles out rapidly. Finally, the anionic solution is added in an amount completely to discharge the pink color from the chloroform layer. This is the end point of the titration.

In the table below, there is a summary of the results obtained by the use of the method of the present invention in connection with illustrative cationic quaternary ammonium compounds, using certain illustrative anionic compounds for the titration. The values obtained were calculated by reference to compound No. 4 as a primary standard and such values are shown in comparison with the values obtained by conventional Volhard and sulfated ash determinations. In this connection, it may be pointed out

that a mean molecular weight was established for the various cationic quaternary ammonium compounds and anionic compounds by the Volhard chlorine titration and the sulfated ash procedure, depending upon the particular compound involved, it being understood that commercial mixtures of the appropriate long-chain alcohols or fatty acids, rather than a single alcohol or a single fatty acid, were employed in the preparation of the cationic quaternary ammonium compounds and anionic compounds. In all cases, also, the cationic quaternary ammonium compounds and the anionic compounds utilized were purified samples of commercially available materials. That is, the inorganic salts present in the commercially available materials were extracted by boiling with 90% aqueous isopropanol followed by recrystallization from a suitable solvent.

In the accompanying drawings, I show a testing kit which is particularly satisfactory for use in the field in accordance with my present invention and wherein Figure 1 represents a perspective view of a carrying case and reagent bottles and testing tube or cylinder disposed therein, and Figure 2 shows the remainder of the reagent bottles and testing tube or cylinder comprising the kit removed from the carrying case.

The carrying case 10 comprises front and rear walls 11 and 12, respectively, side walls 13 and 14, bottom 16 and a cover 17 which is adapted to be closed in any suitable manner as, for example, by means of snaps. The case is partitioned so as to provide a series of pockets or compartments, preferably six in number. As shown in Figure 1, a stoppered bottle 18, a dropper bottle 19 and a graduated testing tube

Table 1,2

No.	Compound ¹	Conventional Analysis	Conventional Value (Mean Molecular Weight)	Value by Anionic-Cationic Titration	Titred Against Compound No.
1.....	$[C_{15}H_{33}-N(CH_3)_3]^+Br^-$ Cetyl trimethyl ammonium bromide	Volhard.....	383	386	2
2.....	$[C_{12}H_{25}-O-CO-CH_2-SO_3]^-HO-C_2H_4-NH_3^+$ Monoethanolamine salt of lauryl sulfoacetate				4
3.....	$C_{12}H_{25}-OSO_3Na$ Sodium lauryl sulfate	Sulfated Ash....	304	307	4
4.....	$[C_{15}H_{31}-CO-O-C_2H_4-NH-CO-CH_2-N \text{ (pyridinium ring)}]^+Cl^-$ N (palmitic acid ester of colamino formylmethyl) pyridinium chloride	Volhard.....	470.5		5, 2, 3
5.....	$C_{12}H_{25}-CO-O-C_2H_4-NH-CO-CH_2-SO_3K$ Lauric acid ester of monoethanolamine sulfoacetamide, potassium salt	Sulfated Ash....	405	397	4
6.....	$[C_{12}H_{25}-N \text{ (pyridinium ring)}]^+I^-$ Lauryl pyridinium iodide	Volhard.....	380.2	338	2
7.....	$[C_{13}H_{27}-CO-O-C_2H_4-NH-CO-CH_2-N(C_2H_5)_3]^+Cl^-$ N (myristic acid ester of colamino formylmethyl) triethylammonium chloride	do.....	440	462.5	2

¹ Commercial long chain alkyl materials were employed in the preparation of the compounds listed above.

² Compound No. 4 (molecular weight 470.5 as indicated by Volhard chlorine titration) was used as a primary standard.

³ Each of the "Compounds" comprises a mixture of homologues, the formula of the listed homologue being that which most closely approaches the mean molecular weight as determined by "Conventional Analysis."

A sample calculation for compound No. 5 is as follows, using, as stated above, compound No. 4 as the standard. A solution was prepared by dissolving 0.4036 gram of compound No. 4 (mean molecular weight by Volhard analysis 470.5) in one liter of distilled water. The normality thereof is

$$\frac{0.4036}{470.5}$$

which equals 0.000859 N. It required 21.30 cc. of a solution of compound No. 5 (containing 0.400 gram per liter of water) to titrate 25 cc. of the aforementioned solution of compound No. 4. Hence,

$$21.30 \times \frac{0.400}{M} = 25.0 \times 0.000859$$

in which case M, the equivalent weight of compound No. 5, equals 397. This value for M, it will be noted, compares very favorably with the value of 405 which was obtained by a sulfated ash determination (a sample of 0.3197 gram of compound No. 5, when ashed in the presence of sulfuric acid, gave 0.0688 gram of potassium sulfate).

or cylinder 21 are disposed, each in one pocket, of the case 10. A stoppered bottle 22, dropper bottle 23 and graduated testing tube 24, shown in Figure 2, are adapted to fit into the remaining pockets of the case and comprise the balance of the testing kit.

The bottle 18 serves to hold a supply of a standard aqueous solution of an anionic compound of known concentration. The dropper bottle 19 serves also to hold the standard solution of the anionic compound which, from time to time, may be replenished from the bottle 18 which, it will be noted, has a substantially larger capacity than does the dropper bottle 19. The graduated testing tube 21 is provided with lines or markings and identifying indicia.

The bottle 22 serves to hold a supply of the fluorescein dissolved, preferably, in ethylene dichloride or carbon tetrachloride or other similar water-immiscible organic solvent. The dropper bottle 23 serves also to hold a solution of the fluorescein which, from time to time, may be replenished from the bottle 22, the latter having a substantially larger capacity than dropper bottle 23. The graduated testing tube 24 is identical with the tube 21.

In the use of the kit, the tube 21 (or 24) is first rinsed and well drained and there is then added thereto, up to the line marked "Test Sample," the aqueous solution of the cationic quaternary ammonium compound to be tested. The indicator solution is then added from dropper bottle 23 by means of the dropper to the line marked "Indicator Solution A," whereupon the tube 21 is stoppered and well shaken. The color of the solution will be pink unless there is no cationic quaternary ammonium compound present or unless the concentration thereof is substantially negligible in the solution being tested. The standard anionic compound solution is then added from dropper bottle 18 up to the line marked 1:12500, the tube 21 is stoppered and shaken about ten times and then allowed to settle. If the lower layer is colorless, the test is complete, showing that the concentration or strength of the cationic quaternary ammonium compound is 1:12500 or less. If, however, the lower layer is still pink, additional anionic compound solution is added up to the line marked 1:6500, the solution shaken and allowed to settle as before. These operations of shaking and allowing to settle are repeated, in each case the solution of the anionic compound being added to the next succeeding line, until the lower layer is substantially colorless. At this stage, the concentration of the cationic quaternary ammonium compound is read directly on the tube 21, at the highest liquid level therein. The concentration of cationic quaternary ammonium compound read on the tube 21 may be translated readily into terms of ounces per gallon or the like and a suitable table may be provided to facilitate this conversion. Thus, for example, a reading of 1:12500 on the tube 21 is equivalent to approximately 1 ounce of cationic quaternary ammonium compound per 100 gallons (U. S.) of water and a reading of 1:2500 on the tube 21 is equivalent to about 1 ounce of the cationic quaternary ammonium compound per 20 gallons (U. S.) of water.

Since the cationic quaternary ammonium compounds are incompatible with soaps and alkaline washing compounds, the tubes 21 and 24, after each test, should be rinsed with plain tap water only, that is, without the addition thereto of soaps or alkaline washing compounds.

In general, the dilute solutions of the anionic compounds or cationic quaternary ammonium compounds which are used as standards should be freshly prepared until their stability has been adequately investigated. In this connection, it will be appreciated that the stability, under ordinary storage conditions, of the various anionic compounds and cationic quaternary ammonium compounds may vary. The ethanolamine salt of lauryl sulfoacetate, in the form of a 0.001 M solution at a pH of 5.65, for example, remains constant titrimetrically for at least three months when stored under usual conditions in an ordinary glass bottle. As a general rule, it is convenient to make up the standard solutions of anionic compounds or cationic quaternary ammonium compounds to a concentration of 0.4 gram per liter, which corresponds to a molarity of 0.001. Other concentrations may, of course, be employed.

I have found that the method of my present invention is well adapted to the determination, in dilute aqueous solutions, of such cationic quaternary ammonium compounds as have an effective lipophile group, particularly an unin-

terrupted aliphatic carbon chain of not less than about 12 carbon atoms. The quaternary nitrogen may be part of a heterocyclic ring, such as a pyridine ring, or it may comprise alkyl, aryl, aralkyl or alkylol substituted ammonia. These criteria must apparently be satisfied, coupled with those set out below in relation to the anionic compounds, in order to obtain accurate or reasonably accurate quantitative determinations.

The anionic compounds should also contain a lipophile group having not less than about 12 carbon atoms, particularly, in an uninterrupted carbon chain, and a hydrophile group in the form of an oxygenated sulphur or phosphorus radical such as a sulfate, sulfonate, orthophosphate, pyrophosphate, tetrophosphate or metaphosphate radical in the form of a salt thereof such as a sodium, potassium, ammonium, ethanolamine or other salt. In general, the optimum pH range for the titration medium is approximately 5.5 to 7.

As I have indicated above, the method of my present invention may be used for the determination of the concentration, in dilute aqueous solutions, of various anionic compounds. In this case, the cationic quaternary ammonium compound is made up in the form of a standard dilute aqueous solution of known concentration and is used to titrate the solution of the anionic compound of unknown concentration. The testing kit, in this case, would be modified only by substituting, in the bottles 18 and 19, a dilute standardized solution of a cationic quaternary ammonium compound for the standardized anionic compound solution. In the titration proper, the end point occurs when the color of the chloroform layers turns from colorless to pink.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. In a method of determining the concentration, in dilute aqueous solutions, of a member selected from the groups consisting of (1) cationic quaternary ammonium compounds containing a chain of not less than about 12 carbon atoms, and (2) anionic compounds of the type which contain an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates, the steps which comprise providing a measured volume of a dilute aqueous solution of a compound falling into one of said groups of compounds, admixing therewith a small proportion of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of a compound falling into the other of said groups of compounds.

2. In a method of determining the concentration, in dilute aqueous solutions, of a cationic quaternary ammonium compound containing a chain of not less than about 12 carbon atoms, the steps which comprise providing a measured volume of the dilute aqueous solution of said cationic quaternary ammonium compound, admixing therewith a substantially lesser amount of a water-immiscible organic solvent and a fraction of a percent of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of an anionic compound of the type which contains an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates.

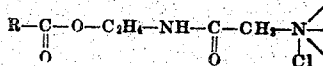
3. In a method of determining the concentration, in dilute aqueous solutions, of a cationic quaternary ammonium compound containing a

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chain of not less than about 12 carbon atoms and wherein the quaternary nitrogen is part of a pyridine ring, the steps which comprise providing a measured volume of the dilute aqueous solution of said cationic quaternary ammonium compound, admixing therewith a substantially lesser amount of a water-immiscible organic solvent, in the form of a chlorinated compound, and a fraction of a percent of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of an anionic compound of the type which contains an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates.

4. In a method of determining the concentration, in dilute aqueous solutions, of a cationic quaternary ammonium compound containing a chain of not less than about 12 carbon atoms, the steps which comprise providing a measured volume of the dilute aqueous solution of said cationic quaternary ammonium compound, admixing therewith a small amount of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of an anionic compound of the type which contains an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates.

5. In a method of determining the concentration, in dilute aqueous solutions, of a cationic quaternary ammonium compound, the steps which comprise providing a measured volume of the dilute aqueous solution of said cationic quaternary ammonium compound, admixing therewith a substantially lesser amount of a water-immiscible organic solvent and a fraction of a percent of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of an anionic compound, said cationic quaternary ammonium compound corresponding to the formula



where



is an aliphatic carboxylic acid acyl radical con-

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taining from 12 to 18 carbon atoms and where the three valence bonds connected to N are directly attached to carbon, and said anionic compound comprising an oxygenated sulfur derivative containing an uninterrupted carbon chain of from 12 to 18 carbon atoms.

6. In a method of determining the concentration, in dilute aqueous solutions, of an anionic compound of the type which contains an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates, the steps which comprise providing a measured volume of the dilute aqueous solution of said anionic compound, admixing therewith a small proportion of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of a cationic quaternary ammonium compound containing a chain of not less than 12 carbon atoms.

7. In a method of determining the concentration, in dilute aqueous solutions, of an anionic compound of the type which contains an uninterrupted carbon chain of not less than about 12 carbon atoms and a radical selected from the group consisting of salts of sulfonates and sulfates, the steps which comprise providing a measured volume of the dilute aqueous solution of said anionic compound, admixing therewith a substantially lesser amount of a water-immiscible organic solvent and a fraction of a percent of dichlorofluorescein, and then titrating with a dilute aqueous solution of known concentration of a cationic quaternary ammonium compound containing a chain of not less than about 12 carbon atoms.

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