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[45] **Mar. 25, 1975**

[54] **METHOD AND APPARATUS FOR DETECTING FREE WATER IN HYDROCARBON FUELS**

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[52] **U.S. Cl.** .... **23/230 HC,** 23/230 R, 23/259, 206/47 A, 252/408
[51] **Int. Cl.. G01n 33/22,** G01n 33/18, G01n 21/06
[58] **Field of Search** ...... 23/259, 253, 230; 252/408; 206/47 A

[56] **References Cited**

UNITED STATES PATENTS

2,429,694	10/1947	King	23/254 X
3,421,857	1/1969	Reichle et al.	23/292 X
3,505,020	4/1970	Caldwell	23/230

Primary Examiner—R. E. Serwin
Attorney, Agent, or Firm—Harold N. Wells; Byron O. Dimmick

[57] **ABSTRACT**

A method and apparatus for detecting the presence of free water in hydrocarbons in which the water reacts with freshly ground fuchsia dye and calcium carbonate having an average particle size of less than 10 microns and a surface area of 5-8 square meters per gram. The reagents are prepackaged in an evacuated glass vial. A sample of the hydrocarbon is admitted to the interior of the evacuated vial by a cannula mounted in a special receptacle adapted to receive the vial. The sample is drawn into the vial by the vacuum and reacts with the dye and carbonate to indicate the presence or absence of free water in the hydrocarbon.

11 Claims, 3 Drawing Figures

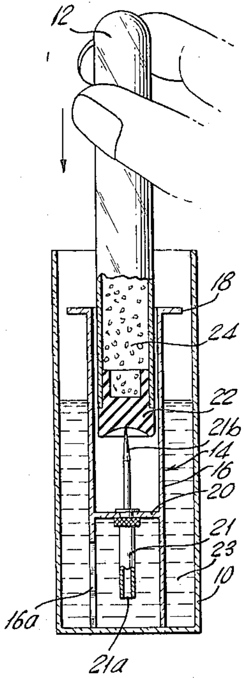


Fig. 1.

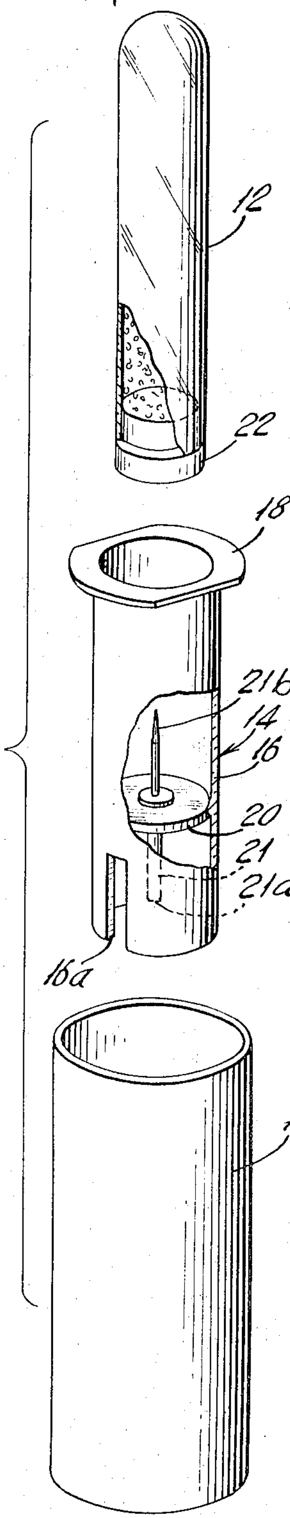


Fig. 2.

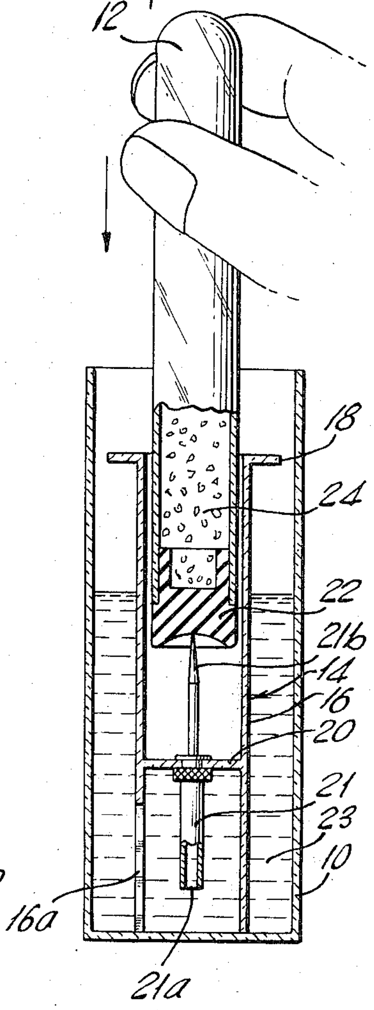
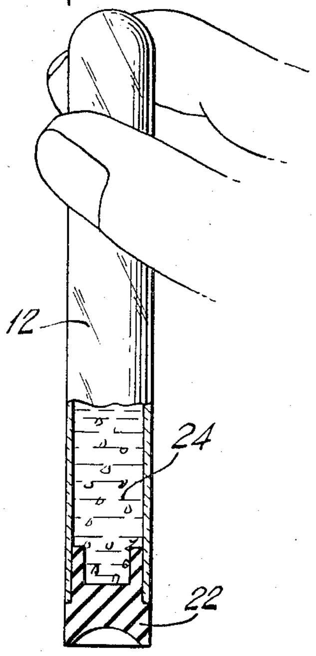


Fig. 3.



METHOD AND APPARATUS FOR DETECTING FREE WATER IN HYDROCARBON FUELS

BACKGROUND OF THE INVENTION

Detection of free (undissolved) water in hydrocarbon fuels is of particular importance with regard to turbojet fuels for aircraft which, operating at high altitudes, are subject to fuel system plugging by ice crystals. To minimize this hazard, it is normal practice to inspect all fuel for the presence of free water as it is being loaded into aircraft. In general, less than about 10 parts per million of free water is satisfactory, but 30 parts per million is too high. Special filter separators are used for removing free water from jet fuels, but testing of individual cargoes is necessary to check their performance. U.S. Pat. No. 3,505,020 disclosed an improved composition for reacting with free water present in jet fuels and producing a pink color which indicates the presence of excessive free water. That composition comprised a small amount of fuchsia dye (3 amino-7(dimethylamino-5-phenylphenazinium chloride) mixed with a major portion of a finely divided anhydrous solid which was selected from the group consisting of calcium carbonate, barium carbonate, barium sulfate, magnesium carbonate, and combinations thereof. The preferred anhydrous solid for the water detection composition is calcium carbonate.

In the prior art, it was disclosed that the dye particles should have a diameter less than 200 microns in order to be effective and, in particular, a weight average particle size of 44 microns was preferred. The particularly preferred composition would limit the dye particle size to under 74 microns with about 40–60 wt. % of the particles having a diameter of less than about 44 microns. The dye is conventionally used in the textile industry and is commonly referred to as Methylene Violet, Basic Violet Five, Color Index 50205, fuchsia and so forth. A further description of the dye may be found in *Color Index, the American Association of Textile Chemists and Colorists, second edition* (1956), at pages 1,635 and 3,414.

Also in the prior art, it was disclosed that the anhydrous solid particles should be less than 10 microns in size and technical grade crystalline powder.

In addition, the portions of anhydrous solid to dye would range between 20 and 10,000 and preferably between 50 and 2,000 parts by weight. One part by weight of dye to about 400 to 1,000 parts by weight of anhydrous solid was particularly preferred.

The reagent mixture would be added to a fuel sample, about 0.05 to 2 grams of the mixture to 100 milliliters of hydrocarbon fuel. The preferred range would be between 0.1 and 0.5 gram of mixture to each 100 milliliters of hydrocarbon.

As indicated in the prior art patent, this mixture gives satisfactory results. However, experience has shown that the method is subject to some practical difficulties. It has been heretofore typical to package the mixed dye and solids in closed containers of a size suitable for testing of individual fuel cargoes. It has been found that deterioration of the reagents occurs over a period of time and shelf life is limited. Accordingly, results after an extended period of storage may be erratic. In addition, it has been found that the composition of the mixture had to be adjusted before being placed into the closed containers in order to provide a uniform response. The

foregoing disadvantages have been overcome by the method and apparatus of the present invention.

SUMMARY OF THE INVENTION

An improved composition for detection of free water in hydrocarbon fuels is obtained by introducing product quality standards for both the anhydrous carbonate and the fuchsia dye not heretofore known. It has been found that the fuchsia dye is more sensitive if it is finely ground immediately prior to being packaged rather than simply being screened and then packaged from the material as received from the supplier. As to the anhydrous carbonate, it has been found that, not only particle size, but effective surface area of the carbonate is important in obtaining a suitable sensitivity. In particular, effective surface areas in the range of 5 to 8 square meters per gram have been found to be preferred for this use. Surface areas greater than this range are generally not sensitive enough and surface areas smaller than the recommended range are too sensitive and neither will produce the desired results.

In the present invention, both carbonate and dye are prepackaged in an evacuated glass vial. The glass vial serves two functions: first, to protect the quality of the chemical reagents used and second, to provide a means for drawing a fuel sample into the vial for reaction with the reagents without ever exposing them to moisture in the air. In order to accomplish the introduction of fuel into the evacuated vial, a special receptacle is provided, mounting a small cannula which pierces a flexible closure at one end of the vial and provides a passageway for the fuel.

In field use, a small sample of fuel is drawn from a fueling line into a small container as an aircraft is being loaded, the receptacle is placed inside the container so that the open end of the cannula is suspended above the bottom of the fuel container, and thereafter the glass vial is inserted into the receptacle. The cannula punctures the flexible closure provided at one end of the vial, thereby providing a passageway between the fuel in the container and interior of the vial. The fuel is drawn in by the vacuum present within the container where it reacts with the reagents, producing a pink color should an excessive amount of free water be present, or remaining clear if less than **10** ppm free water is present.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is an exploded view of the apparatus of the invention prior to its assembly.

FIG. **2** illustrates the apparatus of FIG. **1** in the assembled condition immediately prior to admitting a fuel sample into the glass vial.

FIG. **3** is a vial according to the invention after having received a fuel sample in the manner indicated in FIG. **2**.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. **1** illustrates the three main parts of the apparatus. A small cylindrical container **10** is provided for receiving a small sample of fuel from the loading line. The container **10** has no special requirements except that it should contain sufficient sample to fill the vial **12** which is to be discussed hereinafter. The container **10** should preferably be made of a clear plastic material in order to avoid breakage and to permit observation as to the visual quality of the fuel drawn in, that is, whether it is clear or cloudy and whether it contains any suspended solids. Either of these conditions may indicate a failure of the fuel filter separator which would be located upstream of the sampling point.

The receptacle **14** consists of a cylindrical tube **16** with a flange **18** at one end for convenience in handling and open at either end. Mounted within the tube **16** is a transverse disc **20** which supports a cannula **21** mounted thereon. The cannula **21** provides a narrow passageway and, being blunt at one end **21***a* where fuel is drawn in and pointed at the opposite end **21***b* for piercing the flexible closure of the glass vial **12**. A slot (or other perforation) is provided in the side of the receptacle **14** below disc **20** in order to permit fuel to pass freely into the interior of the tube **16** and be drawn into the blunt end **21***a* of the cannula. It is preferred that the cannula **21** not touch the bottom of the container in order that any extraneous materials which might be drawn in are not admitted to the vial and, therefore, the blunt end **21***a* of the cannula **21** is positioned approximately one-half inch above the bottom of the receptacle **14**.

The improved reagents are enclosed in an evacuated glass vial **12** which is sealed at one end by a flexible closure **22**. This closure **22** serves at least two purposes: first, to prevent breaking of the vacuum which was created in the tube at the time the reagents were sealed inside it and second, to provide a means for ready access of fuel to the reagents when the test is made without ever exposing the reagent to the atmosphere. Use of an evacuated tube permits not only protection of the quality of the reagents, but provides for taking the required amount of fuel sample. In addition, an indication of the quality of the reagents is obtained, for should the vacuum be lost, no fuel sample would be drawn through the cannula, indicating that the quality of the reagents was suspect and should not be used.

In general, the particle size of the fuchsia dye is essentially the same as that indicated in the prior art, but it has been found that freshly ground dye is particularly sensitive and that the sensitivity can be retained by packaging under vacuum. Table I illustrates the significant improvement in sensitivity of the dye when it is freshly ground as compared with the as-received material.

TABLE I

	Free Water Content	
	10 ppm (pass) Color Scale Rdg.	40 ppm (fail) Color Scale Rdg.
Sieve only	0 (white)	½ (trace pink)
Fresh ground	½ (trace pink)	3 (dark pink)

It will be noted that when as received dye is only sieved that only a small color change can be found, whereas the same dye when freshly ground has a much wider color change, which is easily seen and permits some interpolation between 10 ppm and 40 ppm free water. This greater sensitivity can be maintained if the dye is kept sealed and away from moisture and air as in the evacuated vial of the invention. Use of an inert gas in filling the vials will further improve the stability of the dye sensitivity.

As has been mentioned heretofore, it was necessary to empirically adjust the relative quantities of dye and anhydrous solid in order to provide a uniformity of response. It has been found that this irregularity in response of the as received materials was due, not to the particle size which was heretofore thought to be important, but rather to the effective surface area of the solid. It has been found that a relatively low surface area in the range of 0.1 to 4.5 square meters per gram is too sensitive and should not be used. Also, a relatively high surface area in the range of 8.5–10 square meters per gram or more is insensitive and should also not be used. While 5–8m^2/gm is the preferred range, small deviations outside this range - ca. down to 4.5 or up to 8.5m^2/gm could be used. However, added adjustments to the dye to carbonate ratios may be necessary at these outer limits and the desired sensitivity response is bordering on the too sensitive and/or the insensitive areas.

It has been found that a preferred critical range of the order of 5–8 square meters per gram provides good sensitivity and permits the accurate proportioning of dye to solid. The relative sensitivity to surface area of the solid and the merits of restricting the surface area of the solid used to the recommended range will be evident from the data given in Table II below.

TABLE II

$CaCO_3$ Surface Area m^2/gm	Free Water Content 10 ppm (pass) Color Scale Rdg.	40 ppm (fail) Color Scale Rdg.	Comment
0.4	3 (dark pink)	3	too sensitive
1.6	2¾	3	too sensitive
2.78	2 (pink)	2¾	too sensitive
6.5	½ (trace pink)	2½	suitable sensitivity
8.53	½	2½	suitable sensitivity
9.95	0 (white)	1 (light pink)	insensitive

FIG. **2** shows the principal components of the invention in assembled form. Fuel **23** has been placed inside the cylindrical container **10** in a quantity sufficient to more than fill the vial, but leaving some residual amount in the container after the vial has been filled. The receptacle **14** has been placed within the container **10** where it rests on the bottom and fuel is free to pass through the slot **16***a* or other openings placed in the side of the receptacle **14**. The evacuated vial **12** containing the improved reagents **24** has been placed within the receptacle **14** with the point of the cannula **21***b* resting lightly against the flexible closure **22**.

It will be apparent that once the indicated downward motion is made, the cannula **21** will pierce the flexible closure **22** and admit fuel, assuming vacuum within the glass vial, into the vial **12** for reaction with the improved reagents **24**. Once this downward motion has taken place, fuel rushes through the cannula **21** into the glass vial **12** which fills extremely rapidly owing to the presence of the vacuum present inside and quickly mixing the desired amounts of reagent and fuel.

In FIG. **3**, a vial **12**, after it has received a fuel sample, has been withdrawn from the receptacle, the flexible closure **22** sealing behind the cannula **21** as it is withdrawn, thereby retaining the fuel sample therein. The vial **12** may be shaken lightly to mix the reagents and fuel although this is essentially completed by the rapid inrush of fuel as it displaces the vacuum. After a short period, approximately 2 minutes, the color of the dye has developed if the fuel contains free water in excess of 10 parts per million. In general, the quantities of reagent and the sensitivity of the reagents are adjusted so that no color change develops when the free water content is 10 parts per million or below but a pink color develops above that level which may be compared with a known standard. If an excessively dark pink color has developed during the 2-minute period, indicating that more than 30 ppm is present, the fuel must be rejected and reprocessed in order to remove free water present therein. Such standards were used in the results shown in Tables I and II.

The foregoing test is primarily used in the field as a go/no-go test in aircraft fueling. It is within the scope of the invention, however, to package quantities of dye in measured quantities so as to permit a series of such tests to make a more accurate determination of the precise level of water contained. This may be necessary to satisfy both military and commercial standards and to closely measure the quantity of water when a go/no-go test is insufficient.

The foregoing description of the preferred embodiments is for illustration of the invention only and should not be deemed to limit the scope thereof which is defined by the claims which follow.

What is claimed is:

1. An apparatus for detecting the presence of free water in hydrocarbons which comprises in combination:

a. an evacuated tube containing chemicals sensitive to the presence of said free water, said tube being closed at one end and sealed at the other end by a pierceable closure to maintain said vacuum;

b. a receptacle means for receiving said tube of (a);

c. a cannula having an inlet end and an outlet end mounted on said receptacle and disposed to pierce said closure when said tube is inserted into said receptacle, thereby providing a conduit into the evacuated interior of said tube.

2. The apparatus of claim **1** further comprising a container for a sample of said hydrocarbons adapted to receive said tube receptacle means whereby said cannula is enabled to admit hydrocarbons from said container into said tube as urged by the vacuum therein.

3. The apparatus of claim **1** wherein said receptacle means is a cylidner open at both ends and having a transverse partition intermediate said ends for mounting said cannula whereby said cannula serves as a passageway through said partition.

4. The apparatus of claim **3** wherein one of said cylinder ends extends beyond the inlet end of said cannula, thereby preventing said cannula from touching the bottom of said container when said receptacle is inserted therein.

5. The apparatus of claim **4** wherein the cylindrical wall adjacent the inlet end of said cannula contains openings in the sides thereof to admit said hydrocarbon sample when said receptacle is in contact with the bottom of said container and thereby to prevent sampling from the bottom of said container.

6. The apparatus of claim **1** wherein said chemicals for detecting the presence of free water comprise:

a. a finely-divided anhydrous solid having a surface area of 5–8m^2/gm selected from the group consisting of calcium carbonate, barium carbonate, barium sulfate, magnesium carbonate, and combinations thereof;

b. freshly ground fuchsia dye having a particle size between 44 and 74 microns.

7. The apparatus of claim **6** wherein the weight ratio of said solid to fuchsia dye is within the range of 20:1 to 10,000:1.

8. A method for detecting free moisture in hydrocarbons comprising:

a. obtaining a sample of said hydrocarbons in a container;

b. placing in said container a receptacle for receiving a means for withdrawing a portion of said sample, said receptacle being adapted to receive an evacuated sample vial containing moisture sensitive chemical reagents, said sample vial being closed at one end and sealed at the other end with a pierceable closure;

c. piercing said closure with a cannula mounted on said receptacle and admitting a portion of said hydrocarbon through said cannula into said vial as urged by the vacuum therein;

d. reacting said hydrocarbon portion drawn into said vial with said moisture sensitive chemical reagents and thereby producing a color proportional to the free water present in said hydrocarbon portion;

e. comparing the color produced in said hydrocarbon portion drawn into said vial with known standards and thereby determining the amount of free water contained in said hydrocarbon portion.

9. The method of claim **8** wherein said moisture sensitive chemicals comprise:

a. a finely-divided anhydrous solid having a surface area of 5–8m^2/gm and selected from the group consisting of calcium carbonate, barium carbonate, barium sulfate, magnesium carbonate, and combinations thereof;

b. freshly ground fuchsia dye having a particle size between 44 and 74 microns and in a weight ratio to said solid within the range of 1:20 and 1:10,000.

10. A packaged liquid useful for the detection of free water in a liuqid hydrocarbon which comprises a mixture of:

a. a finely divided anhydrous solid having a surface area of from 5 to 8 square meters per gram, said solid being selected from the group consisting of calcium carbonate, barium carbonate, barium sulfate, magnesium carbonate, and mixtures thereof; and

b. freshly ground fuchsia dye having a particle size between 44 and 74 microns;

the weight ratio of said dye to said solid being within the range of 1:20 to 1:10,000;

said mixture having been both prepared and sealed off from contact with moisture and air at the time of grinding said dye.

11. Packaged composition as defined by claim **10** wherein said mixture is maintained in a vacuum.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,873,271 Dated March 25, 1975

Inventor(s) Dale A. Young, Alfred H. Miller and John F. Coburn, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 44, cancel "cylidner" and substitute --cylinder--.

Column 6, line 43, cancel "liquid" and substitute --composition--; line 44, cancel "liuqid" and substitute --liquid--.

Signed and Sealed this

Tenth Day of August 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks