Nov. 29, 1966 J. L. DWYER 3,287,961

DETECTION OF SURFACTANTS

Filed May 6, 1964

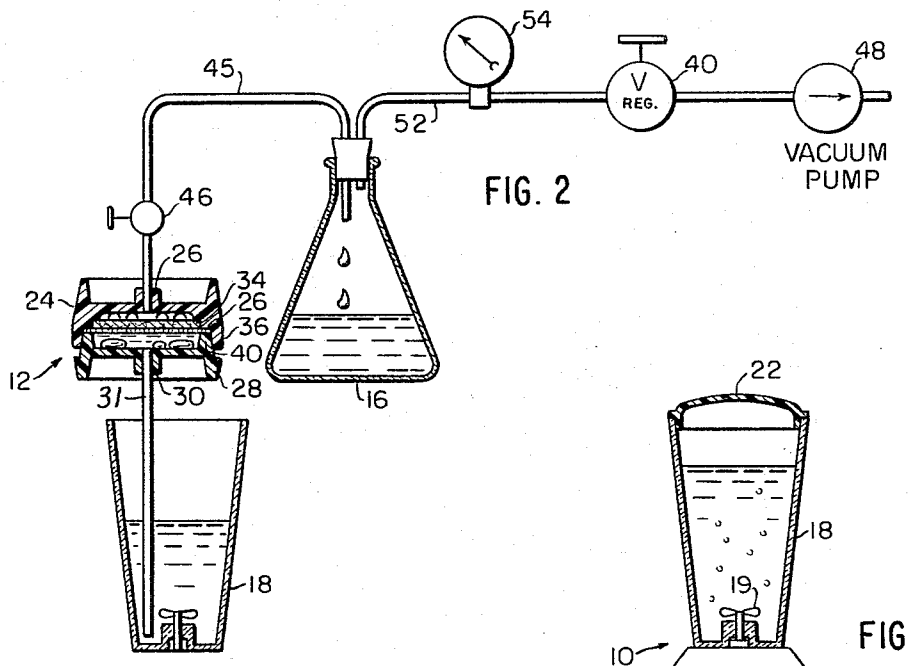



FIG. 2




FIG. 1

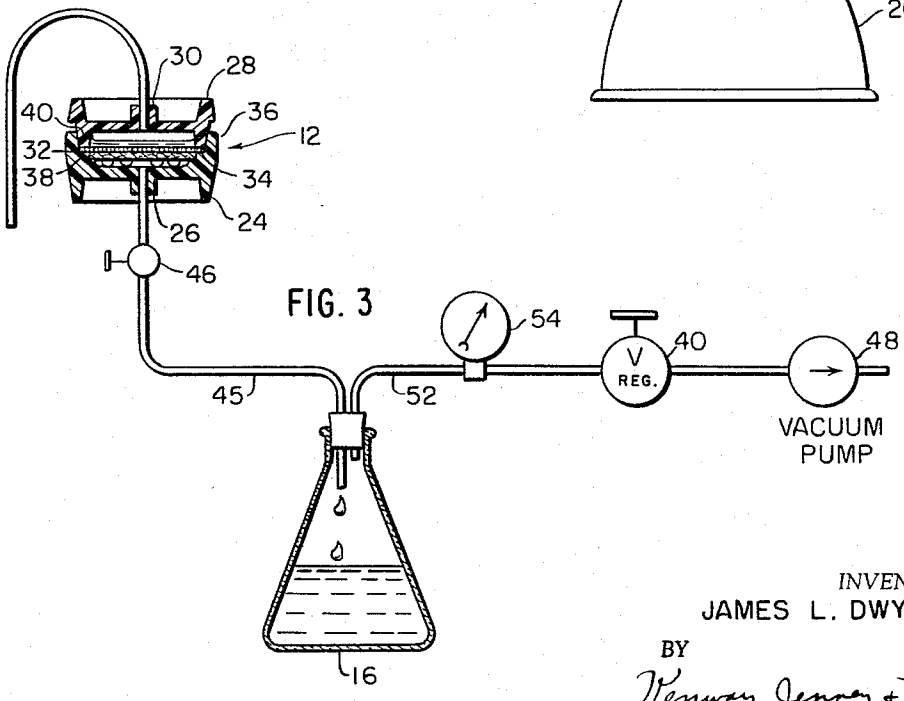



FIG. 3

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United States Patent Office 3,287,961 Patented Nov. 29, 1966



3,287,961

# DETECTION OF SURFACTANTS

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Filed May 6, 1964, Ser. No. 365,246
3 Claims. (Cl. 73—61.1)

This invention relates to the testing of water-immiscible liquids and in particular to the detection of surfactants in liquids such as internal combustion engine fuels.

Surfactants in fuels are generally deleterious because of their effect in causing water and other solid contaminants to become emulsified or suspended whereby impurities are more readily carried by the fuel. Where water has become emulsified, conditions favorable to the growth of microorganisms are also developed, which lead to a great number of difficulties.

The determination of surfactants is complicated by the great number of different chemicals of this type. Chemical tests alone are therefore not reliable, and measurements of behavioral characteristics of a fuel containing entrained water have given better results. Test procedures of this type have developed along two lines, the measurement of specific physical characteristics, such as fuel-water interfacial tension, and simulative tests. Tests of the first type require rather elaborate procedures but are principally hindered in failing to cover all of the factors encountered in actual field performance when surfactants are present.

In the simulative test procedures currently known an attempt is made to duplicate actual conditions encountered in the field and more reliable indication of surfactant effects are obtained. These procedures are not, however, adapted to simple and rapid on-site monitoring of the fuel.

The present invention provides a simplified simulative test which is based on the development of a novel type of separation system and on a procedure whereby that system can be used reliably to determine the presence of surfactants in the fuel and give an indication of the effective amount present.

This invention is based on the discovery that an index to the presence of surfactants in a water immiscible liquid is given by the pressure and time relationship existing when water that has been separated from emulsion with the liquid is forced through a hydrophobic normally water resistant filter. As surfactant will be present in this water, it will pass through a given filter more readily than if the water were free of surfactant, and the degree to which the pressure and/or time required for water to break through provides an effective index to the effective amount of surfactant.

Accordingly, this invention essentially requires that water emulsified in the test liquid be separated out and placed on the hydrophobic filter surface and then forced through the filter while the time and pressure are measured. In the preferred embodiment a given quantity of distilled water is first emulsified into the test liquid to assure that an amount of water sufficient for measurement is present. The water is then separated by drawing or forcing the mixture through a finely porous hydrophobic filter, which will collect and retain the water on the upstream side while permitting the test liquid to pass through. Conveniently the filter surface is held in an inverted or tipped position so that the water does not lie on and eventually cover the surface and interfere with the filtering action. When enough water to cover the filter surface has been separated on the upstream side of the filter, the apparatus is positioned with the filter forming the bottom surface



covered by water, and the pressure difference is regulated to force the water through in a measured time interval.

The hydrophobic filter may be any of a number of finely porous hydrophobic materials known to the art, which may be selected on the basis of the known characteristic of materials of this type to retain water while permitting organic liquids to pass. A suitable filter will have pore size and hydrophobic characteristics not only effective to remove the water when the mixture is passed through at low pressure differential, but also that permits the water to pass through under a higher, yet measurable, pressure differential. In the preferred procedures the filtration pressure differential is created by a vacuum pump and limited to about 30 inches of Hg; therefore, a material through which pure water will flow at something less than 30 inches of Hg is required.

The preferred hydrophobic filter material is a commercially available membrane filter, consisting typically of precipitated cellulose esters, having a void volume of about 80% and a pore size of 0.80 microns. Treatment of the membrane filter with methyl chlorosilanes results in the formation of a polysiloxane surface coating which renders this material extremely water repellent. A membrane of this type will permit the passage of pure water when a pressure differential of about 24 inches of Hg has been reached.

A useful adjunct to the test procedure, which is also provided by this invention, facilitates the determination of the initial passage of water, by the appearance of contrasting color at the downstream side of the filter. For this purpose a porous backing member that has been impregnated with a water soluble, oil insoluble dye is provided to support the downstream side of the filter. The breakthrough of water results in the solution of some of the dye and the appearance of a cooled liquid at the filter outlet when the time and pressure conditions necessary for breakthrough have been reached.

A representative and preferred embodiment of this invention is described below. Reference is made to the accompanying drawings in which

FIG. 1 is a schematic cross-section of a blender representative of the first step in the method of this invention;

FIG. 2 is a schematic cross-section in elevation illustrating the step of withdrawing a sample of emulsified water and test liquid to collect a sample of emulsion water;

FIG. 3 is a similar view illustrating the final test procedure in which the collected emulsion water is caused to break through the filter under measured conditions of pressure and/or time.

The apparatus for practicing this invention includes a high speed mixer **10** (see FIG. 1) and a filtration system (see FIGS. 2 and 3) comprising a filtration unit **12** and a variable vacuum source connected to the filtration unit **12** through a filtrate collection vessel **16**.

The high speed mixer **10** may be a conventional blender in which a mixing jar **18** having an agitator blade **19** projecting through its bottom engages with a motor driven power unit **20**. A cover **22** for the jar **18** should be provided.

The filtration unit **12** is typically formed of a bottom dish **24** having a drainage port **26** and a close fitting cover **28** having an inlet port **30**, and contains a microporous filter film **32** arranged for filtration between the inlet and outlet ports. The filter film is conveniently supported on a porous support pad **34** which provides for drainage of filtrate from beneath the filter film.

The bottom dish **24** is preferably molded from a transparent plastic and is formed with an upright circular wall **36** terminating at its lower edge in an annular shoulder **38** which supports the margin of the filter film **32**. The

cover **28** is similarly formed of a transparent plastic and includes a downwardly extending side wall **40** frictionally engaging the upright wall **36** and terminating in an edge abutting the margin of the filter film to hold it securely against the shoulder **38**.

The porous support pad **34** is retained within the annular shoulder **38**, with its top surface generally coplanar therewith, on a channelled bottom surface which provides for the flow of filtrate to the outlet port **26**.

In the preferred filter unit the support pad is a fibrous material such as blotting paper that has been impregnated with a water soluble dye such as methylene blue. This may be prepared simply by taking a standard grade of blotting paper, e.g. Hurlbut Grade 469, and dipping it into an aqueous solution containing 0.5 gram per liter of methylene blue and then drying the paper. Discs cut of this to fit within the bottom area of the filter unit provide for the development of a blue color once water has broken through the hydrophobic filter.

A convenient technique for producing hydrophobic filters consists in treating a commercially available cellulose ester membrane filter, suitably one having a pore size of 0.80 micron, e.g. Millipore type AA, with a commercial organo halogenosilane as described by Patnode U.S. Patent No. 2,306,222. The resulting filter is thoroughly hydrophobic and well suited for use in the practice of this invention.

Filtration is effected by applying a vacuum to the filter unit **12** through a suction line **45**, which connects to the outlet port **26** through a valve **46** and leads to the collection vessel **16**. A variable vacuum within the vessel **16** is maintained by a vacuum pump **48** which connects through an adjustable vacuum regulator valve **50** to the vessel, by a line **52**, into which is tapped a vacuum gauge **54**.

In the preferred test procedure 500 cc. of the test liquid is placed in the thoroughly clean blender jar **18** and 5 cc. of distilled water are added. With the cover **22** in place the blender is operated at high speed for about one minute, during which some, but generally not all, of the water becomes entrained or emulsified in the test liquid.

After the water and test liquid have been thoroughly agitated, a sample is drawn through the filter housing **12**, as illustrated in FIG. 2, by means of a tube **31** extending from the inlet port **30** into the water-test liquid mixture. In this operation the filter housing **12** is inverted so that the water separated from the mixture does not lie on the filter film **32**.

In this operation the vacuum is adjusted to about 10.5 inches of Hg and the valve **46** in the outlet line from the filter unit is opened slowly so that the water-test liquid mixture is introduced gradually to prevent a vapor lock. When the filter unit is full of liquid the valve is opened entirely and all but about one-half inch of the liquid in the blender jar filtered through the filter unit.

During the filtration process water emulsified in the test liquid is removed and collects in the top (lower portion) of the filter unit.

After the water has collected in an amount at least sufficient to cover the filter film the filter unit is righted, preferably gradually with the vacuum applied so that the test liquid which will generally float on top of the water, will be drawn off through the filter film before the water covers it.

When the unit has been righted a timer should be started, so that, if water will come through under the existing pressure (10.5 in. Hg) the measure of its time may be had. If water does not appear in one-half minute the vacuum is increased by 2 inches (or any other convenient increasement) then again increased if water does not appear within one-half minute, and so on until the passage of water is noted.



The pressure and time required for the passage of water provides a convenient index determinative of the presence of surfactants. Their presence is indicated whenever the breakthrough of water occurs at a lower pressure differential or in a shorter period of time than when pure distilled water is forced through the filter. In the embodiment described above, pure water will pass through the filter under a vacuum of about 24 inches of Hg, a detectable amount appearing in from one-half to one and one-half minutes. If then a test sample of water collected from the water-test liquid mixture penetrates the filter more readily, i.e. in shorter time or under a lower pressure differential, the presence of a measurable quantity of surfactants is indicated. It has been found that as little as 0.05 part per million of some surfactants can be detected.

Although this invention has been described with specific reference to its preferred embodiment, it is contemplated that obvious modifications will occur to those skilled in the art and familiar with the principles of this disclosure and that such may be made without departing from the scope of this invention.

It is apparent for instance that water emulsified in the test liquid may be separated by techniques other than filtration such as by centrifuging and that the water collected from the test liquid could be forced through the hydrophobic filter by the application or generation of a positive pressure. In addition while the presence of a water soluble colored substance in the support underlying the filter provides a convenient indication of the passage of water colorless substance e.g. ionizable salts, which can be detected chemically or electrically are also suitable for the same purpose.

Having thus disclosed my invention and described its preferred embodiments in detail, I claim and desire to secure by Letters Patent:

**1.** The method of testing a water immiscible liquid for the presence of surfactants comprising adding water to said liquid and mixing it therewith, separating water from said liquid and placing it on a hydrophobic filter then applying a sufficient pressure differential across said filter to force the water therethrough, and measuring said pressure.

**2.** The method of testing water-immiscible liquids for the presence of dissolved surfactants comprising adding water to said liquid and agitating sufficiently to suspend the water therein, filtering the liquid and suspended water through a water repellent filter to separate the water by collecting it at the upstream side of the filter in an amount sufficient to cover the filter, then applying a pressure differential to the water on said filter sufficient to force the water therethrough, and measuring said pressure differential.

**3.** Apparatus for testing water immiscible liquids comprising a vacuum pump, having a vacuum conduit, a variable vacuum reducing valve in said vacuum conduit whereby a variable reduced pressure can be produced in said conduit, a vacuum gauge in said conduit responsive to said variable pressure, and a filter containing a hydrophobic filter film and having an inlet at one side of said film and an outlet at the other side of said film connected by said outlet to said conduit, said housing being positionable to permit or prevent water in said housing to cover said film.


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DAVID SCHONBERG, *Primary Examiner.*

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,287,961 November 29, 1966

James L. Dwyer

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 10, for "permits" read -- permit --; line 35, for "cooled" read -- colored --; column 3, line 55, after "jar" insert -- is --; column 4, line 59, after "filter" insert -- housing --.

Signed and sealed this 12th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents