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METHOD FOR DETECTING DISPERSED WATER IN HYDROCARBONS

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The present invention relates to improved methods for determining the presence of water in hydrocarbons and more particularly relates to a new and improved test for detecting trace quantities of dispersed water in aviation turbo-jet fuels and similar hydrocarbon oils.

Aircraft powered by turbo-jet engines must operate at extreme altitudes during sustained flight in order to obtain maximum fuel utilization. At the temperatures prevailing at such altitudes, any water dispersed in turbo-jet fuel quickly freezes to form ice crystals which may block lines, screens and orifices in the fuel system. Losses in engine power and, in some cases, "flame-outs" may result. Such difficulties do not arise from the presence of dissolved water in turbo-jet fuels. In order to minimize the hazards engendered by dispersed water, the airlines and military services require that aviation turbo-jet fuel be inspected for the presence of dispersed water before it is transferred into the fuel tanks of an aircraft. The inspection procedure generally employed involves the collection of fuel samples from the refueling tank trucks on the flight line and the visual examination of those samples for haze. The presence of haze in such samples is generally indicative of dispersed water but the absence of haze does not necessarily mean that no free water is present. Experience has shown that such fuels may contain considerable quantities of dispersed water even though no haze is discernible and that the conventional inspection procedure is therefore not reliable.

Efforts have been made in the past to develop a simple and yet reliable test which can be used to determine the presence and amount of dispersed water in turbo-jet fuels. Because such a test must be susceptible of being carried out quickly with a minimum of equipment, must be accurate and dependable, must not be distorted by the presence of water dissolved in the fuel, and must be applicable to fuels containing a wide variety of additives approved for use in turbo-jet fuels, such efforts have not been successful heretofore.

The present invention provides a new and improved method for detecting the presence and extent of dispersed water in aviation turbo-jet fuels and similar hydrocarbons which is considerably more reliable than methods employed for this purpose in the past. The method of the invention is accurate to within about 10 parts per million of dispersed water in a range of from about 20 to about 500 parts per million or higher and its accuracy is not adversely affected by the presence of dissolved water or additives commonly employed in turbo-jet fuels and similar oils. The method may be quickly carried out without extensive laboratory equipment, gives results which are readily susceptible of interpretation, and is inexpensive to use.

In accordance with the invention, it has now been found that the presence and extent of dispersed water in aviation turbo-jet fuels and similar hydrocarbon oils can be quickly and easily determined by contacting a sample of the oil with a small amount of a particular mixture of a finely-divided, water-soluble, solid anhydrous dye and a finely-divided solid capable of taking up or adsorbing

any water present in the sample. The presence of dispersed water in a sample of turbo-jet fuel or a similar oil treated in this manner results in a change in the color of the mixed solids in the sample. No such change occurs if the sample contains only dissolved water. The contacting step is preferably carried out by agitating a fuel sample containing the mixed solids and then permitting the solids to settle. The intensity of the color of the solids after settling is directly proportional to the amount of free water dispersed in the sample. By agitating equal amounts of the mixed solids with an unknown sample and prepared samples of a similar oil containing measured amounts of dispersed water, allowing the solids in each sample to settle, and comparing the colors of the solids, the dispersed water content of the unknown sample can be determined with an accuracy of plus or minus ten parts per million or better.

The mechanisms involved in the method of the invention are not fully understood. It is thought, however, that the color change produced is not due to chemical reactions involving the dye and instead is a physical phenomenon. Apparently a portion of the water-soluble, oil-insoluble dye dissolves if dispersed water is present in the oil and the resulting dye solution is adsorbed by the finely-divided solid to produce a color change from white or gray to pink or red within about three minutes or less. If no dispersed water is present, no dye is dissolved and hence the pristine color of the mixed solids remains. Since the amount of dye dissolved and adsorbed is proportional to the amount of water dispersed in the sample, the relative intensity of the pink color produced accurately reflects the water content. It has been observed that both the dye and finely-divided solid used are highly critical and hence other mechanisms may also be involved.

The finely-divided, water-soluble, oil-insoluble dye which is employed in carrying out the method of the invention is the sodium salt of o-cresolsulfonphthalein. The unreacted dye, o-cresolsulfonphthalein itself, is insoluble in water and hence is unsatisfactory for purposes of the invention. The sodium salt is employed as an acid-base indicator in analytical chemistry and is readily available from commercial sources as an anhydrous powder. It is in this form that the dye is used.

As pointed out above, the use of the sodium salt of o-cresolsulfonphthalein is critical to the success of the method of the invention. It has been found that other dyes, including those used as acid-base indicators, are not satisfactory for purposes of the invention for several reasons. Water-soluble organic dyes in general readily react with additives employed in turbo-jet fuels and similar hydrocarbon oils as rust inhibitors, antioxidants, dispersants and the like, thus consuming the dye so that no color change occurs or producing a colored reaction product which masks the true color of the solids used in the test. Many such dyes have an additional disadvantage in that they rapidly change color when stored with the finely-divided solid employed as the second constituent of the mixed solids. Such premature color change makes the mixture useless for test purposes.

The second constituent of the mixture of finely-divided solids employed in carrying out the method of the invention is finely-divided anhydrous barium carbonate. This compound is essentially insoluble in both hydrocarbon oils and in water. It has been found that closely related salts such as sodium carbonate and barium sulfate give misleadng results when used in conjunction with the dye and hence are unsatisfactory for purposes of the invention. Similarly, inert materials such as ground glass have been found ineffective. The barium carbonate employed may be in the form of a finely-divided technical

grade crystalline powder readily available from commercial sources but must be anhydrous.

The dye and the barium carbonate are generally added to the fuel sample to be tested in a ratio of from about 25 to about 500, preferably about 50 to about 250, parts by weight of the carbonate of each part of the dye. The exact ratio of carbonate to dye may be varied over a considerable range depending upon the particular method which is to be employed for determining a change in color or color intensity. The use of about 1 part of dye and about 100 to 200 parts of adsorbent has been found to be particularly effective. The amount of the dye-carbonate mixture added to the sample to be tested may be varied widely, from about 0.1 to about 5 grams per 100 milliliters of oil for example. In general, however, it is preferred to add from about 0.25 to about 1 gram of the mixed solids to each 100 milliliters of oil to be tested.

The color of the solids in the oil sample after settling may be compared with predetermined standards in a number of different ways. Visual examination will indicate whether a color change from white to pink or red indicative of the presence of dispersed water has occurred and will in most cases serve as a means for comparing color intensities to determine the amount of dispersed water contained by the sample being tested. More accurate determinations can be made, however, by employing a colorimeter for collating the color of the solids in the sample with predetermined standards. The Lovibond colorimeter is satisfactory for this purpose and a number of other similar devices may also be used. Such devices are widely employed for determining the colors of hydrocarbon oils, waxes, asphalts, and similar materials and their construction and operation will be familiar to those skilled in the art.

In employing the method of the invention for determining the dispersed water content of a hydrocarbon oil sample, a dye-carbonate mixture is first prepared by mixing from about 25 to about 500 parts of finely-divided anhydrous barium carbonate with 1 part of an anhydrous sodium salt of o-cresolsulfonphthalein. Samples of the fuel to be tested and a similar fuel saturated with water but containing no dispersed water are prepared. Varying amounts of water are added to the samples of saturated fuel containing no dispersed water to serve as standards. Uniform amounts of the dye-barium carbonate are then added to the fuel sample of unknown water content and to each of the standard samples. All of the samples are shaken vigorously for 10 to 30 seconds and the solids in the sample bottles are then allowed to settle. The color of the solids in the sample of unknown water content is then compared with the colors of the standard samples. The comparison may be done either by visual examination or by means of a suitable instrument. The dispersed water content of the unknown sample is indicated by the water content of the standard which most nearly matches the unknown sample in color intensity.

The test method of the invention may also be employed for determining in the field whether aviation turbo-jet fuels and similar hydrocarbon oils have dispersed water contents which meet predetermined specifications. In order to do this, a dye-barium carbonate mixture, an oil sample containing slightly more dispersed water than permitted by the applicable specification, and an oil sample containing slightly less water than the specification permits are prepared. Equal amounts of the dye-barium carbonate mixture are added to a sample of the oil to be tested and to each of the samples containing known amounts of dispersed water. Each sample is then agitated and the solids therein are permitted to settle. The intensity of the color of the solids in the test sample is compared with that of the solids in the two prepared samples and from this comparison it is determined whether the fuel contains more or less than the allowable quantity of water. Again the color intensity comparison may be carried out by visual examination but more accurate results can be obtained by means of a colorimeter or a similar device.

In lieu of preparing standard samples each time an unknown is tested in the manner described above, in many cases it may be preferable to photograph standard samples and employ the pictures as a basis for comparison in future tests. This procedure somewhat simplifies carrying out the test under field conditions.

For ease of handling and in order to facilitate the carrying out of the method of the invention, it will generally be found convenient to package the mixed dye and barium carbonate in capsules or ampules of polyethylene or a similar material. Each capsule may contain sufficient mixed dye and carbonate for one test. For relatively short periods of time it is sufficient to store the capsules in a tightly closed glass jar. Where the capsules are to be stored for extended periods of time or under severe weather conditions, it may be preferred to maintain them in a sealed vessel in the presence of a desiccant.

The exact nature and objects of the invention are further illustrated by the following examples.

EXAMPLE 1

A dye-barium carbonate mixture was prepared by mixing 100 grams of dry anhydrous barium carbonate with 1 gram of the sodium salt of o-cresolsulfonphthalein. The mixture was stored in a tightly-closed, dry container. An anhydrous sample of aviation turbo-jet fuel was saturated by placing the sample in a closed cabinet having 100% humidity for a period of about 16 hours. Water was added from a microburet to a series of marked dry bottles. The amount of water added increased 2 milligrams from bottle to bottle. 100 milliliters of the water-saturated fuel were then added to each bottle containing water. One hundred milliliters of a fuel of unknown water content was added to a marked, dry bottle. All bottles were then closed with tight covers and shaken vigorously for 3 minutes. To each bottle was added 0.5 ± 0.02 gram of the previously prepared dye-barium carbonate mixture. The bottles were shaken for 15 seconds and the solids were permitted to settle. It was noted that the solids which settled in the bottles were all essentially pink in color but that the color varied in intensity in proportion to the dispersed water content. The color intensity of the solids in the bottle containing the unknown sample was compared with that of each of the samples containing known amounts of dispersed water to determine the water content of the unknown sample. Similar tests were carried out using a mixture of 1 part of the sodium salt of o-cresolsulfonphthalein and 200 parts of barium carbonate and the same results were obtained.

A comparison between the amount of dispersed water as determined from the tests described above and the amount of water which had actually been added to the samples is shown below.

Table I

Sample	H_2O Added,[1] p.p.m.	H_2O Found, p.p.m.
A	30	30
B	50	50–55
C	90	90–95
D	150	140

[1] H_2O added to JP–4 aviation turbo-jet fuel saturated with water.

From the above table it can be seen that the results of the test indicated very closely the actual water content of the fuel samples. The slight variations between the actual water content and the water content indicated by the test could have been reduced had a colorimeter been employed for matching the colors. Six different turbo-jet fuels and kerosines derived from widely different crude

oils were tested in like manner and in each case the test method accurately indicated the dispersed water contents.

EXAMPLE 2

A "go-no go" test to determine whether samples of an aviation turbo-jet fuel contained more or less than 30 parts per million of dispersed water was carried out. A quantity of a fuel essentially identical to the fuel to be tested was saturated with water in the manner described in the preceding example. A 100 milliliter sample of the fuel thus saturated, a 100 milliliter sample of the saturated fuel to which have been added 3 milligrams of water and a 100 milliliter sample of the saturated fuel to which had been added 10 milligrams of water were prepared. These 3 samples were shaken for 3 minutes to disperse the water in the fuel. To each sample was added 0.5 gram of a test mixture consisting of 1 part of an anhydrous sodium salt of o-cresolsulfonphthalein and 100 parts of barium carbonate. The samples were shaken 15 seconds and allowed to stand for about 5 minutes. The solids which settled in the sample containing 10 milligrams of dispersed water had a pink-violet color. The solids in the sample containing only the saturated fuel were white. The sample containing 30 parts per million of dispersed water was intermediate between these two and had a faint pink color. Colored pictures were taken of the solids at the bottom of each bottle and developed.

Samples of 6 different aviation turbo-jet fuels to which had been added 50 parts per million of water were placed in dry bottles. The dye-barium carbonate mixture was added to each bottle, about 0.5 ± 0.2 gram being used. The bottles were then shaken and allowed to stand for 5 minutes. The color intensity of the solids at the bottom of each bottle was compared to that of the solids in the 3 pictures previously taken to determine whether the fuel samples contained more or less than 30 parts per million of dispersed water. In each case the solids after settling had a pink color intermediate between the color in the picture of the sample containing 30 parts per million of dispersed water and the color in the picture of the sample containing 100 parts per million of dispersed water.

EXAMPLE 3

Tests similar to those described in the preceding examples were carried out using samples of aviation turbo-jet fuels containing various additives commonly used in such fuels. Parallel tests were run on samples of the fuel containing no dispersed water and samples containing 40 parts per million of dispersed water. The additives employed in carrying out these tests were those approved for use in military aviation fuels in accordance with Military Specification MIL–I–25017, Qualified Products List QPL–25017–3 of May 15, 1956, and supplements thereto. The results obtained in these tests are shown in the following table.

Table II

TEST FOR WATER IN FUELS CONTAINING ADDITIVES

Fuel Sample	Additive	Conc. of Additive in the Fuel (p.p.m.)[1]	Color of Solid Reagent	
			No Dispersed Water	40 p.p.m. Dispersed Water
A	Santolene C	20	White	Pink.
B	Alox L 1846	20	do	Do.
C	Kontall 77	30	do	Do.
D	Gulf Agent 178	20	do	Do.
E	Nasul A.S.	45	do	Do.
F	Nasul E.D.S.	50	do	Do.
G	Texaco Aircraft Fuel Inhibitor.	50	do	Do.
H	Unicor	40	do	Do.
I	Paradyne HO–4	120	do	Do.

[1] All additives used in concentrations 5–25% higher than the ones that normally would be used in the fuels.

From the foregoing, it can be seen that none of the approved additives interfered with the carrying out of the test for dispersed water. Since the samples tested contained the additives in concentrations somewhat higher than those normally used, any tendency for the additives to react with the test reagents would have been accelerated. At least one of these additives is almost always present in turbo-jet fuel and hence any test for dispersed water must not be distorted by presence of the additives.

EXAMPLE 4

Further tests similar to those described in the preceding example were carried out using, in place of the mixture of barium carbonate and the sodium salt of o-cresolsulfonphthalein, a mixture of the sodium salt of o-cresolsulfonphthalein and finely-divided anhydrous sodium carbonate. The dye and sodium carbonate were used in the same proportions employed in the previous examples and the test procedure employed was the same. A commercial JP–4 aviation fuel meeting the requirements of Military Specification MIL–F–5624 D was employed in the tests. This fuel contained 8 pounds of Santolene C, an approved rust inhibitor referred to in the preceding example, per 1000 barrels. Despite the fact that measured amounts of free water had been added to samples of the fuel saturated with water by storing them in an atmosphere containing 100% humidity for 16 hours, the tests carried out with the mixture of sodium carbonate and the sodium salt of o-cresolsulfonphthalein gave negative results, indicating falsely that no dispersed water was present. Parallel tests using the barium carbonate-sodium salt of o-cresolsulfonphthalein correctly indicated the dispersed water content of the fuel.

EXAMPLE 5

Still further tests were carried out in which a mixture of anhydrous sodium carbonate and anhydrous phenolphthalein was substituted for the barium carbonate-sodium salt of o-cresolsulfonphthalein mixture of the invention and samples of JP–4 fuel containing dispersed water were employed. Again it was found that false negative results were obtained. The actual dispersed water content of the fuel was indicated to within ± 10 parts per million when the barium carbonate-sodium salt of o-cresolsulfonphthalein was used.

EXAMPLE 6

Separate test mixtures of the sodium salt of o-cresolsulfonphthalein with ground glass and with barium sulfate were prepared in order to further determine the criticality of using barium carbonate. In each case the mixture changed color during storage under essentially moisture-free conditions before it could be used in test work, indicating that such mixtures are ineffective for purposes of the invention. By way of contrast, similarly stored mixtures of the invention showed no such change. Moreover, mixtures of barium carbonate and the sodium salt of o-cresolsulfonphthalein packaged in capsules and contained in glass jars with a desiccant have been maintained in humidity cabinets in an atmosphere of 100% humidity for periods in excess of two months without any change in color and have given accurate test results when subsequently used.

Although the test method of the present invention has been described herein primarily in conjunction with the determination of dispersed water in turbo-jet aviation fuels, it will be understood that the method is equally applicable for detecting the presence of dispersed water in solvents, gasolines, kerosines, heating oils and a wide variety of other hydrocarbon oil products of similar properties. The method is particularly adapted for determining the dispersed water contents of hydrocarbons boiling in the range between about 75° F. and about 750° F.

What is claimed is:

1. A method for detecting the presence of dispersed

water in hydrocarbons which comprises contacting said hydrocarbons with a minor amount of a mixture of a finely-divided anhydrous sodium salt of o-cresolsulfonphthalein and finely-divided anhydrous barium carbonate whereby said mixture undergoes a change in color in the presence of free water.

2. A method as defined in claim 1 wherein said sodium salt of o-cresolsulfonphthalein and said barium carbonate are present in said mixture in a ratio of from about 50:1 to about 250:1 by weight.

3. A method as defined by claim 1 wherein said hydrocarbons are contacted with from about 0.1 to about 5 grams of said mixture per 100 milliliters.

4. A method for determining the presence and extent of dispersed water in hydrocarbons which comprises adding a minor amount of a mixture of one part by weight of a finely-divided anhydrous sodium salt of o-cresolsulfonphthalein and from about 25 to 500 parts by weight of finely-divided anhydrous barium carbonate to a sample of said hydrocarbons; agitating said sample; permitting solids to settle in said sample; and comparing the color of the settled solids with predetermined standards.

5. A method as defined by claim 4 wherein the color of said settled solids is compared with predetermined standards by means of a colorimeter.

References Cited in the file of this patent

"Determination of Minute Traces of Water by Use of Methylene Blue," Nesh, Analytical Chemistry, vol. 27, No. 11, November 1955, pages 1842, 1843.