

## ONE DAY FUEL OIL STABILITY

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### UOP Method 413-82

#### SCOPE

This method is for determining the accelerated storage stability of distillate fuel oils. It is valuable for providing rapid information which indicates the tendency of an oil to form sediment and color in storage. It is also very useful as a rapid screening test for evaluating various inhibitors that may be added to promote the storage stability of fuel oils.

#### OUTLINE OF METHOD

The fuel oil is heated at 100 C (212 F) in the presence of oxygen for 16 hours. The entire sample is filtered and the amount of sediment collected is weighed. The color or transmittance of the oil is also measured before and after the heating period for comparative purposes.

#### DISCUSSION

There is no general agreement on what constitutes satisfactory criteria for determining stability of distillate fuels. Some believe that a filterability test, such as UOP Method 359, should be the important criterion, especially if dispersant-type fuel oil additives are used. Others regard total sediment as the only important criterion. Color and soluble gum are also often regarded as important. Other tests emphasize the light absorptivity of the sediment. This test method takes total sediment and color as the criteria for stability.

The method employed herein, uses heat to accelerate the degradation of the distillate oil. However, it should be noted that there is considerable indication<sup>1</sup> that heating does not produce results that are directly relatable to what will actually happen with some distillate oils during storage at ambient temperatures. The subject method, adapted from one suggested by Gyrath, et al.<sup>2</sup> has been adopted because it is quick and convenient. It also differentiates nicely between the various additives and is usually useful in suggesting the concentrations of inhibitors to be added to fuel oils for long-term storage tests.

#### APPARATUS

*Induction period apparatus*, as shown in the drawing, consists of an enclosed water bath (1), or, a multiple thereof, each containing 4 stainless steel oxygen pressure vessels (2), having inside dimensions of 54-mm (preferred) to 57-mm diameter by 210-mm height, sufficient to hold a 250-mL Pyrex sample bottle (3). The head (4) of each pressure vessel has a square-groove joint and fits closely (with a gasket) onto the pressure vessel. The head is held in place by 6 bolts with hexagonal nuts. The flange at the top of the pressure vessel is tapped and a stainless steel tube connects the pressure vessel with a pressure recorder (5).

**IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).**

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The recorder may be operated with 1 to 4 points, allowing a different color pen for each pressure vessel in the bath. A manifold (6) connects each pressure vessel to the pressure-regulated oxygen tank (7), via individual valves (17), and is provided with a 690 kPa (100 psi) relief valve (14), a block valve (15) and a vent valve (16). Heating or cooling is achieved by introducing either steam (18) or cold water (19) into the water bath (1). Note: All references to pressures are pounds per square inch gauge. (Assembled apparatus is not commercially available at this time.)

*Balance*, capable of weighing to 0.1 mg

*Bottles*, 250-mL, Pyrex, constructed from 51-mm OD standard wall tubing, 190-mm high with a 22-mm ID neck opening, UOP Inc., or equivalent

*Cell*, spectrophotometer 40-mm path length, UV silica, Beckman Instruments Inc., Cat. No. 580016, or equivalent

*Colorimeter*, according to ASTM D 1500, Fisher Scientific Co., Cat. No. 13449, or equivalent

*Cylinder*, graduated, 200-mL

*Desiccator*, with aluminum plate

*Dish*, Petri, borosilicate glass, 60-mm diameter

*Filter holder*, stainless steel, "Millipore Hydrosol" filter holder, Millipore Corp., No. XX 20 047 20, or equivalent

*Flask*, filtering, with side arm, 500-mL

*Gaskets*, 0.79-mm thick, asbestos composition, for pressure vessels. John Crane Packing Co., gasket No. 888, or equivalent, has been found suitable when used in conjunction with the Teflon gasket lubricant

*Gasket lubricant*, Teflon, aqueous suspension, used to coat gasket and to prevent sticking. Available from DuPont, as Teflon No. 30 TFE, or equivalent, resin aqueous dispersion, in 4-L quantities only. Gaskets are soaked for 5 minutes in a 1:1 aqueous solution, then allowed to air dry, hanging from a horizontal rod, for at least 3 hours.

*Oven*, gravity convection, capable of operation at  $150 \pm 1$  C

*Pipet*, automatic, 150-mL capacity, SGA Scientific Inc., Cat. No., JP-6875 (special order), or equivalent

*Pipet*, Mohr, long tip Pyrex, 2-mL graduated, 0.01-mL divisions, Sargent-Welch Scientific Co., Cat. No. S-69585-EE, or equivalent

*Pump*, vacuum, heavy duty, Sargent-Welch Scientific, Cat. No. S-71380, or equivalent

*Recorder*, Foxboro, Model 47986, 4 pen spiral type, range 0-1380 kPa (0-200 psi), or equivalent

*Regulator*, oxygen, 2- stage, delivery pressure range 28-690 kPa, (4-100 psig), Matheson Co., Cat. No. 3104-540, or equivalent

*Shaker*, Junior Orbit Shaker, Lab Line Instruments Inc., Model 3520 with Model 3520-6 platform, or equivalent

*Spectrophotometer*, single beam, Bausch & Lomb, Model 710, or equivalent. Modify cell holder, if required, to accept a 40-mm cell.

*Thermometer*, ASTM Saybolt viscosity thermometer No. 22 C, having a range of 95 to 103 C (204 to 218 F) as prescribed in ASTM Specification E 1.

## REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

*Acetone*, dry

*Gum solvent*, Toluene-Acetone-Methanol (TAM) mixture, 1:1:1 by volume

*n-Heptane*, 99% minimum purity, available from Phillips Petroleum Co., or equivalent

Hydrochloric acid, 1:1 by volume

*Membrane filter discs*, 0.8  $\mu\text{m}$ , 47-mm diameter, white, plain, MF-Millipore, or equivalent

*Oxygen*, extra dry, 99.6% minimum purity. **CAUTION**, use extreme care in the handling of compressed oxygen.

## PREPARATION OF APPARATUS

(Refer to drawing)

Thoroughly clean all pressure vessels (2), heads and gasket seats (4) with acetone soaked paper towels so that they are free from any traces of gasoline, oil or gum deposits. Be certain that all traces of acetone are removed from the pressure vessels, etc. Using brief bursts of oxygen from the oxygen tank (7), set at 690 kPa (100 psi) according to gauges (9) and (10), make sure that the oxygen inlet to the pressure vessel via the oxygen manifold (6) is dry and free of any traces of acetone. Clean several Pyrex sample bottles to remove any trace of lead deposits, which may remain from leaded fuels, using 1:1 HCl. Following this, remove detergents, oils and gums by using gum solvent (TAM) followed by first an acetone and then a distilled water rinse with subsequent drying at 105 C.

## PREPARATION OF SAMPLES

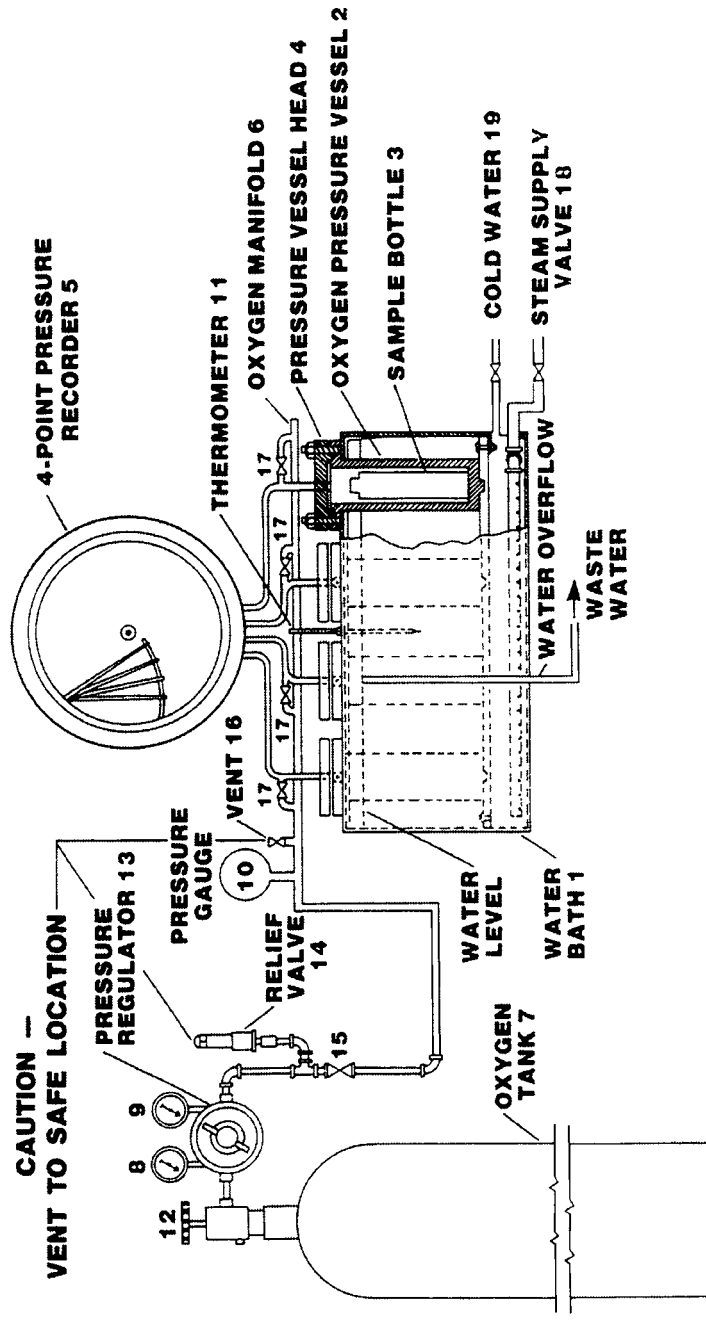
Filter a sufficient amount of the fuel sample through a 0.8  $\mu\text{m}$  filter and measure the color by ASTM D 1500. If desired, also determine the percent transmission with a spectrophotometer at 650 nm in a 40-mm cell using water as the reference. Report these data for the unaged fuel. The sample bottle is charged from an automatic pipet, or a 200-mL graduated cylinder, with 150 mL of the filtered fuel to be tested and is placed into the center of the pressure vessel well (2).

If the stability of a given fuel is to be tested with an inhibitor-additive, which is normally added in the range of 2 to 100 wt-ppm, accurately prepare 100 mL of a 1-2 wt/vol-% toluene solution of the additive. Follow this by a secondary toluene dilution in such a way that an aliquot of one-to-two mL from a graduated 2-mL pipet, when added to 150-mL of gasoline, produces the desired wt-ppm additive concentration. Simultaneously agitate up to 9 sample bottles containing the fuel with the additive by using the Junior Orbit Shaker on a safe rotational speed setting for about 10 minutes. Place the sample bottles into the pressure vessel wells (2).

## PROCEDURE

### Oxygen Purge

Bring all oxygen pressure vessels containing the test samples to a uniform temperature of 15-25 C (59-77 F) by turning on the cold water supply valve (19) at the water bath (1) of the pressure vessel apparatus and



UOP Induction Period Pressure vessel Bath

allowing the water to exit freely at the stand pipe overflow for approximately 60 minutes. Install the circular charts in the pressure recorder for later leak testing of the pressure vessels.

Position a new Teflon-coated gasket on the pressure vessel head (4), cover the pressure vessel (2) with the lid and hand tighten all nuts. Using a manually operated torque wrench at 275 kPa (40 psi), or a pneumatic wrench with an air supply at 620 kPa (90 psi), first tighten opposite nuts lightly, then firmly to 275 kPa (40 psi).

Flush out the air in the pressure vessel with oxygen by closing the exhaust vent (16), opening the oxygen tank valve (12), block valve (15), needle valves (17), and slowly adjusting the cylinder regulator valve (13) until the gauges (9) and (10) read 690-705 kPa (~ 100 psi). Next, close block valve (15) and slowly release all pressure by opening the exhaust vent (16), slowly reopen the block valve (15) to repressurize the system with oxygen, and repeat two more purges as described. Finally, leaving the pressure vessels pressurized under  $690 \pm 4$  kPa ( $100 \pm 0.5$  psi) of oxygen, by closing all valves (17) as well as block valve (15), slowly open exhaust vent (16) until the pressure gauge (10) indicates zero kPa, and check for pressure vessel leaks by observing the pens of the pressure-recorder (5). The recorder pen should show no change over a period of 15 minutes.

After a leak free system is assured, slowly release the oxygen in each pressure vessel by opening all needle valves (17) until atmospheric pressure is reached. Then close the needle valves (17) for all pressure vessels to “lock in” the sample.

### Start-up

Close the cold water supply valve (19). Fully open the steam supply valve (18) to heat up the water bath as rapidly as possible. Record the start-up time (steam valve opened). When the bath has reached a temperature of 100 C (212 F) in about 20 minutes time, adjust the steam supply valve so that a reduced steam supply will assure a temperature of 100 C for the duration of the test as indicated by the thermometer (11). (The maximum obtainable temperature may vary slightly depending on the barometric pressure.) Allow the samples to heat or age for 16 hours at 100 C under oxygen at atmospheric pressure.

### Shutdown

Record the bath temperature from the thermometer (11). Turn off the steam supply valve (18) and open fully the cold water valve (19). Only after the pressure vessel lids are cold to the touch, *slowly* release all pressure vessel pressures by opening the exhaust vent (16) and all valves (17), until the pens of recorder (5) indicate zero pressure. Unlock and remove the samples.

### Sample Analysis

Briefly swirl the sample bottles and quantitatively vacuum filter the sample through a  $0.8 \mu\text{m}$  filter disc weighed to the nearest 0.1 mg, which is held in the Millipore filter holder. Remove the filtered sample from the filtering flask and, without delay, measure the color by ASTM Method D 1500 and, if desired, the percent transmission in a spectrophotometer at 650 nm in a 40-mm cell using water as a reference. Replace the filtering flask and rinse the sample bottle with three, 25-mL portions of *n*-heptane, transferring each wash to the filter holder. Thoroughly wash the filter disc and holder with *n*-heptane, using vacuum, to remove all traces of fuel oil. Any residual fuel oil remaining on the filter will influence sediment measurement. Discard the *n*-heptane filtrate.

Place the filter in an appropriately labeled Petri dish and dry the filter in an oven for 1/2 hour at 95 C (*do not exceed 95 C*). Remove the dish and filter from the oven and cool in a desiccator for one hour. Weigh the filter disc to the nearest 0.1 mg. Correct sediment weights for a moisture blank by processing a filter blank in exactly the same fashion, heptane washing and drying, as a sample. A blank should be determined for every four oil samples analyzed.

## CALCULATIONS

Report the ASTM color, as well as the percent (%) transmission, if desired, for the filtered fuel before heating (unaged fuel), and again after heating (aged fuel). An approximation of the ASTM color may be obtained by converting the % transmission using the attached *Correlation Table*. The quantity of sediment formed, in mg, after heating of the aged fuel is calculated for 100 mL of sample as follows:

$$\text{Sediment, mg/100 mL} = \frac{(A - B)}{1.5}$$

where

**A** = mass of sediment in sample, mg

**B** = mass of sediment in blank, mg

**Correlation Table**

| <b>ASTM<br/>D 1500<br/>Filter Value</b> | <b>% Transmittance<br/>650 nm, 40-mm Cell</b> |
|-----------------------------------------|-----------------------------------------------|
| 0.5                                     | 88.5-100.0                                    |
| 1.0                                     | 82.5- 88.4                                    |
| 1.5                                     | 76.3- 82.4                                    |
| 2.0                                     | 70.1- 76.2                                    |
| 2.5                                     | 64.1- 70.0                                    |
| 3.0                                     | 58.0- 64.0                                    |
| 3.5                                     | 51.8- 57.9                                    |
| 4.0                                     | 45.7- 51.7                                    |
| 4.5                                     | 39.8- 45.6                                    |
| 5.0                                     | 33.6- 39.7                                    |
| 5.5                                     | 27.6- 33.5                                    |
| 6.0                                     | 21.5- 27.5                                    |
| 6.5                                     | 15.2- 21.4                                    |
| 7.0                                     | 9.2- 15.1                                     |
| 7.5                                     | 3.2- 9.1                                      |
| 8.0                                     | 0.0- 3.1                                      |

## INTERPRETATION OF RESULTS

Although a dark color has no functional effect on a fuel oil, most refiners prefer to market a light-colored oil. Color, and especially color degradation, is considered an index of the stability of an oil although no direct relationship has been established. When various oils or inhibitors are tested, the one that has the least color degradation is considered superior.

Total sediment formed is taken as an important criterion of fuel oil stability because it correlates roughly with field performance. The physical characteristics of the sediment may be more important than the actual weight of the sediment in causing filter and injector plugging in home furnaces. However, the practice of determining total weight of the sediment is an accepted technique whereas no measurement of other physical properties is generally applied. The sediment formed in long-term storage, then, is usually the criterion of fuel oil stability.

## PRECISION

The estimated standard deviation (esd) for the sediment determination and % transmission based on the indicated replicates is shown below. Duplicate results by the same operator should not differ by more than the amounts shown in the allowable difference column (95% probability).

| <u>Sample Type</u> | <u>Number of Replicates</u> | <u>Sediment Level, mg/100 mL</u> | <u>Sediment esd, mg/100 mL</u> | <u>Sediment Allowable Difference, mg/100 mL</u> |
|--------------------|-----------------------------|----------------------------------|--------------------------------|-------------------------------------------------|
| Distillate         | 7                           | 2                                | 0.05                           | 0.16                                            |

| <u>Sample Type</u> | <u>Number of Replicates</u> | <u>Range of % Transmission</u> | <u>esd</u> | <u>Allowable Difference, % Transmission</u> |
|--------------------|-----------------------------|--------------------------------|------------|---------------------------------------------|
| Light Cycle Oil    | 8                           | 35-43                          | 2.7        | 9.0                                         |

## TIME FOR ANALYSIS

The elapsed time for one analysis is 19 hours. The labor requirement is 1.25 hours.

The test is normally run in duplicate. In groups of 10 determinations the elapsed time is 22 hours and the labor requirement, per sample, is 0.55 hour.

## REFERENCES

1. Am. Chem. Soc., Symposium on Additives in the Petroleum Industry, *Ind. Eng. Chem.* **48**, 1885-1903 (1956)
2. Gyrath, F. W., Dunn, F. R., Jr., and Smith, A. C., Jr., "One Day Stability Test for Distillate Fuel", *Preprints of General Papers, Div. of Pet. Chem., Am. Chem. Soc.* 3 No. 3, 135-144 (Sept. 7-12, 1958) Chicago, Illinois
3. Christian, J. G., Chiantella, A. J., Johnson, J. E., and Carbart, H. W., *Ind. Eng. Chem.* **50**, 1153 (1958)
4. "Static Electricity Can be a Fire Hazard" F. F. Group, National Safety Council-Research Newsletter, Aug., 1979, Page 4. Operational and Environmental Safety Division, U.S. Dept. of Energy.

## **SUGGESTED SUPPLIERS**

Bausch & Lomb, 340 Melvin Dr., Northbrook, IL 60062  
Beckman Instruments, Inc., Scientific Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634.  
E. I. DuPont & Co., Wilmington, DE 19898.  
Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143.  
Foxboro Co., 2050 Algonquin Rd., Schaumburg, IL 60195.  
John Crane Packing Co., 6400 Oakton St., Morton Grove, IL 60053.  
Lab Line Instruments Inc., Lab-Line Plaza, Melrose Park, IL 60160.  
Matheson Co., P. O. Box 96, Joliet, IL 60434  
Millipore Corp., Bedford, MA 01730.  
Phillips Petroleum Co., Special Products Div., Bartlesville, OK 74004.  
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077  
SGA Scientific Inc., 770 N. Church Rd., Elmhurst, IL 60126.  
UOP Inc., Process Div., 20 UOP Plaza, Des Plaines, IL 60016.