Designation: D 3709 – 89 (Reapproved 1999)

An American National Standard

Standard Test Method for
Stability of Water-in-Oil Emulsions Under Low to Ambient Temperature Cycling Conditions[1]

1. Scope

1.1 This test method is intended to indicate the stability of water-in-oil emulsions when subjected to temperature cycling changes between ambient temperature and –18°C (0°F).

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent[2]

3. Summary of Test Method

3.1 A 100-mL sample contained in a graduated 100-mL cylinder is placed in a cooling box at −18°C (0°F) for 16 h and then allowed to stand at room temperature for 8 h. This cycling procedure is repeated to give a total of nine cycles, except that the fifth cycle is one of 64 h at −18°C (0°F), 8 h at room temperature. At the completion of the cycling procedure the sample is examined for the amount of free oil and free water separated. In addition, water contents of the sample at specified levels in the upper and lower layers of the sample are also obtained.

4. Significance and Use

4.1 This test method indicates the ability of the emulsion to withstand mild to moderately severe winter conditions of use and storage. Generally this significance would be limited to conditions where the emulsion reaches a minimum temperature of −18°C (0°F).

5. Apparatus

5.1 *Cold Box*—A thermostatically controlled freezer or cold box capable of being maintained at −18 ± 1.5°C (0 ± 3°F).

5.2 *Graduated Cylinder*—A stoppered 100-mL glass cylinder graduated in 1.0-mL increments. The stopper should have a vent groove to prevent vacuum or pressure build-up during the test.

5.3 *Pipet*, 10-mL glass.

5.4 *Microsyringe*, 0.05-mL glass with a fixed needle, No. 19 gage, point style No. 3.

5.5 *Glass Vials*, approximately 30-mL size.

6. Preparation of Sample

6.1 To ensure uniformity of the sample, it should be mixed thoroughly before removing the quantity required for the test. Vigorous hand shaking or mechanical mixing for 3 to 5 min is recommended for litre-size containers or less.

6.2 Special difficulties arise in mixing and withdrawing representative samples from large containers. This is due to the nature of water-in-oil emulsions that are two-phase systems as distinct from truly homogeneous systems. Vigorous mechanical stirring for an extended period is the best means of achieving homogeneity. However, for unstable emulsions that have been in storage for some time there is no satisfactory way to obtain a representative sample.

7. Procedure

7.1 After careful preparation of the sample to ensure homogeneity (described in Section 6), transfer 100 mL to a graduated 100-mL cylinder. Insert the vented stopper.

7.2 Place the cylinder in the cold box at −18 ± 1.5°C (0 ± 3°F) for a period of 16 h. Withdraw the cylinder from the cold box and allow to stand at room temperature, 21 ± 3°C (70 ± 5°F), for a period of 8 h.

7.3 Repeat the cycling procedure as in 7.2 for three more cycles.

7.4 Replace the cylinder in the cold box for a period of 64 h. Withdraw and allow to stand at room temperature for 8 h.

7.5 Repeat the cycling procedure as in 7.2 for four more cycles, except that during the final cycle, the period at room temperature is limited to 3 h instead of 8 h before making observations.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.N0.02on Industrial Applications.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

7.6 Observe and record the following:

7.6.1 The amount of oil separated, percent volume and

7.6.2 The amount of water separated, percent volume.

7.7 By means of a 10-mL pipet, withdraw aliquots in the following order.

7.7.1 With the pipet tip located exactly at the 80-mL mark, slowly withdraw a 10-mL sample and transfer to a small glass vial. This is designated as the *upper layer* sample.

7.7.2 With the pipet tip located exactly at the *15*-mL mark, slowly withdraw a 10-mL sample and transfer to a small glass vial. This is designated as the *lower layer* sample.

7.8 Determine the water content, as percent weight, of the upper layer and lower layer samples, after shaking, by the procedure given in the Annex. Use a 0.05-mL sample transferred from the vials by means of a glass microsyringe.

8. Report

8.1 Report the results as follows:

8.1.1 Oil separation, percent volume,

8.1.2 Water separation, percent volume,

8.1.3 Upper layer water content, percent weight, and

8.1.4 Lower layer water content, percent weight.

9. Precision and Bias [3]

9.1 The precision (see Note 1) of this test method is dependent on the degree of instability brought about by the temperature cycling process.

9.1.1 *Type I—Stable Emulsions (Procedures A and B)*:

9.1.1.1 *Precision*—The precision of the method as determined by the statistical examination of interlaboratory test results is as follows.

9.1.1.2 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty. (See Table 1.)

9.1.1.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty. (See Table 1.)

NOTE 1—Precision limits are based on a round-robin test program carried out in Technical Division N in 1977 using invert emulsion samples with water contents between 35 and 50 % (weight). Eleven cooperators tested five samples representing highly stable, borderline, and unstable emulsions.

9.1.2 *Type II—Unstable Emulsions*— Results can vary widely on samples which show any degree of instability brought about by temperature cycling and no precision limits can be set.

9.1.3 *Bias*—No bias statement is possible because there is no absoute value. The results are interpretable only with respect to this test.

10. Keywords

10.1 emulsions; water separation; oil separation

TABLE 1 Repeatability and Reproducibility For Type 1 Only

	Free Oil, %	Free Water, %	Difference in % Water Content Upper Layer Versus Lower Layer
Repeatability	1	1	3
Reproducibility	2	2	3

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[3] The results of the cooperative test program, from which these values have been derived, are available from ASTM Headquarters. Request RR:D02-1158.

ANNEX

(Mandatory Information)

A1. MODIFIED TEST METHOD D 1744 (KARL FISCHER)

A1.1 Scope

A1.1.1 This test method covers the determination of water in the concentration from 50 to 1000 ppm in liquid petroleum products.

A1.2 Significance and Use

A1.2.1 Knowledge of the water content of petroleum products can be useful to predict quality and performance characteristics of the product.

A1.3 Modified Procedure

A1.3.1 To obtain weight of sample, weigh the syringe to 0.1 mg before and after introducing the sample to the titration vessel.

A1.3.2 Use a 1 part xylene to 2 parts methanol mix as the solvent instead of a 3 parts chloroform to 1 part methanol mix.

NOTE A1.1—**Warning:** Flammable. Harmful if inhaled. Skin irritant on repeated contact. Eye irritant. Aspiration hazard.

A1.3.3 A water equivalent of 2.0 to 2.5 mg of water/mL for the Karl Fischer reagent is recommended.

A1.4 Precision and Bias

A1.4.1 The precision of Test Method D 1744 with this solvent system is now under study by Subcommittee D.02.03.

A1.4.2 No bias statement is possible because there is no absolute value. The results are interpretable only with respect to this test.