Designation: ~~D7946 – 14~~ D7946 – 19

Standard Test Method for
Initial pH (i-pH)-Value of Petroleum Products[1]

This standard is issued under the fixed designation D7946; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. ~~Scope~~ Scope*

1.1 This test method covers procedures for the determination of initial pH (i-pH) in new and in-service lubricants.

NOTE 1—In new and used oils, the constituents that may be considered to have characteristics influencing the i-pH value include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents. "Initial" is used to differentiate from aqueous systems. The analysis is terminated after a defined time interval whenever equilibrium conditions, as known for pH measurements in aqueous systems, are not reached (see 3.1.1.2)

1.2 This test method is used to indicate relative changes that occur in oil during use under oxidizing conditions or due to contamination by blow-by gases of combustion processes of biogases regardless of the color or other properties of the in-service lubricants. Although the initial pH is made under definite equilibrium conditions, the test method is not intended to measure an absolute acidic property that can be used to predict performance of oil under service conditions. No general correlation between corrosion of non-ferrous bearing metals and initial pH value is known.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

3.1.1 *initial pH (i-pH), n*—the measure of the hydrogen ion (H+) concentration when a fixed sample amount of lubrication oil is dissolved into a fixed volume of solvent and using a specified detection system.

3.1.1.1 *Discussion*—

This test method expresses the amount of dissociated acidic components as i-pH of a sample in a mixture of toluene and propan-2-ol to which a small amount of water has been added.

3.1.1.2 *Discussion*—

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Liquid Fuels and Lubricants.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

The measured i-pH is called initial since the original definition of the pH-scale depends on aqueous solutions. Its application to organic solutions will not give stable electrode potential for all types of samples. A potential reading after a defined time is used in those cases instead.

4. Summary of Test Method

4.1 The oil sample is dissolved in solvent mixture and the i-pH value is measured using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are measured manually or automatically.

5. Significance and Use

5.1 New and used petroleum products may contain acidic constituents that are present as additives, degradation products formed during service, such as oxidation products or components formed from combustion gases. The i-pH-value is a measure of the amount of acidic substances and their acidity defined under the conditions of test. The i-pH-value is used as a measure of lubricant degradation in service.

5.2 The corrosiveness of acidic components depends on their concentration and acidity. The i-pH-value is a measure of the amount of dissociated acidic components with the potential of corrosiveness towards metals.

5.3 Since a variety of oxidation and blow-by products contribute to the i-pH-value, this test method cannot be used to predict corrosiveness of oil or blends under service conditions against metallic components. No general correlation is known between i-pH-value and the corrosive tendency of blends or oils toward metals.

6. Apparatus

6.1 *pH-Meter*—Meter, a voltmeter or a potentiometer, that will operate with an accuracy of ±0.005 V and a sensitivity of ±0.002 V over a range of at least ± 0.5 V when the meter is used with the electrodes specified in 6.2 to 6.4 and when the resistance between the electrodes falls within the range from ~~0.2 MΩ~~0.2 MΩ to 20 ~~MΩ.~~MΩ. The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching, with a grounded lead, any part of the exposed surface of the glass electrode, the glass electrode lead, the stirrer, or the meter.

NOTE 2—A suitable apparatus could consist of a continuous-reading electronic voltmeter designed to operate on an input of less than 5 × 10^{-12} ~~A,~~ A, when an electrode system having a resistance of ~~1000 MΩ~~1000 MΩ is connected across the meter terminals and provided with a metal shield connected to the ground, as well as a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from any external electrostatic field.

6.2 *Sensing Electrode,* Standard pH, suitable for nonaqueous media.

6.3 *Reference Electrode,* Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1 mol/L to 3 mol/L LiCl in ethanol.

6.4 *Combination Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. The combination electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, for example, ~~1~~1 mol ~~mol/L to~~L to 3 mol/L LiCl in ethanol. These combination electrodes shall have the same response or better response than a dual electrode system. They shall have movable sleeves for easy rinsing and addition of electrolyte.

6.5 *Variable-Speed Mechanical Stirrer,* a suitable type, equipped with a propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution. A propeller with blades 6 mm in radius and set at a pitch of 30° to 45° is satisfactory. A magnetic stirrer is also satisfactory. If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the meter reading during the course of the determination.

6.6 *Beaker,* 250 mL capacity, made of borosilicate glass or other suitable material.

6.7 *Beaker,* 100 mL, or suitable capacity, made of borosilicate glass or other suitable material.

6.8 *Stand,* suitable for supporting the electrodes, and stirrer.

NOTE 3—An arrangement that allows the removal of the beaker without disturbing the electrodes and stirrer is desirable.

6.9 *Graduated Cylinder,* 100 mL, or dispensing device capable of delivering 70 mL ± 0.5 mL.

6.10 *Pipette,* 2.0 mL, Class A.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as being equivalent.

7.3 Alternative volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

7.4 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water that meets the requirements of either Type I, II, or III of Specification D1193.

7.5 *Ethanol,* (**Warning—**Flammable and toxic, especially when denatured.)

7.6 *Lithium Chloride,* LiCl.

7.7 *Lithium Chloride Electrolyte*—Prepare a 1 mol/L to 3 mol/L solution of lithium chloride (LiCl) in ethanol.

7.8 *Propan-2-ol, Anhydrous,* (less than 0.1 % H_2O). (**Warning—**Flammable.) If adequately dry reagent cannot be procured, it can be dried by distillation through a multiple plate column, discarding the first 5 % of material distilling overhead and using the 95 % remaining. Drying can also be accomplished using molecular sieves such as Linde Type 4A, by passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent.

NOTE 4—It has been reported that, if not originally inhibited against it, propan-2-ol can contain peroxides. When this occurs, an explosion is possible when the storage of the vessel or other equipment such as a dispensing bottle, is near empty and approaching dryness.

7.9 *Toluene,* (**Warning—**Flammable.)

7.10 *Commercial Aqueous pH 4 and, pH 7 Buffer Solutions*—These solutions shall be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

8. Electrode System

8.1 *Preparation of Electrodes*—When a Ag/AgCl reference electrode is used for the determination and it contains an electrolyte which is not 1 mol/L to 3 mol/L LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve, ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

8.2 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent then with water, and dip them into a pH 4 aqueous buffer solution. Read the mV value after stirring 1 min. Remove the electrodes and rinse with water. Dip the electrodes into a pH 7 aqueous buffer. Read the mV value after stirring 1 min. Calculate the mV difference. A good electrode system will have a difference of at least 162 mV (20 °C to 25 °C). If the difference is less than 162 mV, lift the sleeve of the electrode and insure electrolyte flow. Repeat the measurements. If the difference is still less than 162 mV, clean or replace the electrode(s).

8.3 When the sensing electrode and the reference electrode are separate, one pair of electrodes shall be considered as one unit. If one or the other is changed, it shall be considered as different pair and shall be retested.

8.4 *Maintenance and Storage of Electrodes*—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining repeatable potentials, since contamination may introduce uncertain erratic and unnoticeable liquid contact potentials.

NOTE 5—See Appendix X1 for a possible procedure to check the electrode performance.

8.5 Clean the glass electrode at frequent intervals based on use and type of samples being analyzed (not less than once every week during continual use) by immersing in non-chromium containing, strongly oxidizing cleaning solution. The reference electrode shall be cleaned periodically when in use or when a new electrode is installed. Drain the reference electrode at least once each week and refill with the fresh LiCl electrolyte as far as the filling hole. Ensure that there are no air bubbles in the electrode liquid. If air bubbles are observed, hold the electrode in a vertical position and gently tap it to release the bubbles. Maintain the electrolyte level in the reference electrode above that of the liquid in the sample beaker or vessel at all times.

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[3] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.