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

1. 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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*—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.

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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 to 20 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, when an electrode system having a resistance of 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 mol/Lto 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